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\* \* \* \* \* Welcome to STN International \* \* \* \* \*

NEWS	1		Web Page for STN Seminar Schedule - N. America
NEWS	2	JAN 02	STN pricing information for 2008 now available
NEWS	3	JAN 16	CAS patent coverage enhanced to include exemplified prophetic substances
NEWS	4	JAN 28	USPATFULL, USPAT2, and USPATOLD enhanced with new custom IPC display formats
NEWS	5	JAN 28	MARPAT searching enhanced
NEWS	6	JAN 28	USGENE now provides USPTO sequence data within 3 days of publication
NEWS	7	JAN 28	TOXCENTER enhanced with reloaded MEDLINE segment
NEWS	8	JAN 28	MEDLINE and LMEDLINE reloaded with enhancements
NEWS	9	FEB 08	STN Express, Version 8.3, now available
NEWS	10	FEB 20	PCI now available as a replacement to DPCI
NEWS	11	FEB 25	IFIREF reloaded with enhancements
NEWS	12	FEB 25	IMSPRODUCT reloaded with enhancements
NEWS	13	FEB 29	WPINDEX/WPIDS/WPIX enhanced with ECLA and current U.S. National Patent Classification
NEWS	14	MAR 31	IFICDB, IFIPAT, and IFIUDB enhanced with new custom IPC display formats
NEWS	15	MAR 31	CAS REGISTRY enhanced with additional experimental spectra
NEWS	16	MAR 31	CA/CAPLUS and CASREACT patent number format for U.S. applications updated
NEWS	17	MAR 31	LPCI now available as a replacement to LDPCI
NEWS	18	MAR 31	EMBASE, EMBAL, and LEMBASE reloaded with enhancements
NEWS	19	APR 04	STN AnaVist, Version 1, to be discontinued
NEWS	20	APR 15	WPIDS, WPINDEX, and WPIX enhanced with new predefined hit display formats
NEWS	21	APR 28	EMBASE Controlled Term thesaurus enhanced
NEWS	22	APR 28	IMSRESEARCH reloaded with enhancements
NEWS EXPRESS FEBRUARY 08 CURRENT WINDOWS VERSION IS V8.3, AND CURRENT DISCOVER FILE IS DATED 20 FEBRUARY 2008			
NEWS	HOURS	STN Operating Hours Plus Help Desk Availability	
NEWS	LOGIN	Welcome Banner and News Items	
NEWS	IPC8	For general information regarding STN implementation of IPC 8	

Enter NEWS followed by the item number or name to see news on that specific topic.

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\* \* \* \* \* STN Columbus \* \* \* \* \*

FILE 'HOME' ENTERED AT 11:08:35 ON 13 MAY 2008

=> FILE CASREACT

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.21

0.21

FILE 'CASREACT' ENTERED AT 11:09:20 ON 13 MAY 2008

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FILE CONTENT:1840 - 10 May 2008 VOL 148 ISS 20

New CAS Information Use Policies, enter HELP USAGETERMS for details.

\*\*\*\*\*  
\*  
\* CASREACT now has more than 13.8 million reactions \*  
\*  
\*\*\*\*\*

Some CASREACT records are derived from the ZIC/VINITI database (1974-1999) provided by InfoChem, INPI data prior to 1986, and Biotransformations database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=>

Uploading C:\Program Files\Stnexp\Queries\GH.str product

L1 STRUCTURE UPLOADED

=>

Uploading C:\Program Files\Stnexp\Queries\GH.str reactant/reagent

L2 STRUCTURE UPLOADED

=> S L1 FULL

FULL SEARCH INITIATED 11:10:08 FILE 'CASREACT'

SCREENING COMPLETE - 9102 REACTIONS TO VERIFY FROM 2415 DOCUMENTS

100.0% DONE 9102 VERIFIED 602 HIT RXNS 281 DOCS

SEARCH TIME: 00.00.02

L3 281 SEA SSS FUL L1 ( 602 REACTIONS)

=> S L3 AND LITHIUM METAL

25160 LITHIUM

51803 METAL

106 LITHIUM METAL

(LITHIUM(W)METAL)

L4 1 L3 AND LITHIUM METAL

=> S L3 AND LITHIUM

25160 LITHIUM

L5 86 L3 AND LITHIUM

=> S L3 AND LI  
10305 LI

L6 59 L3 AND LI

=> D L4 IBIB ABS CRD 1

L4 ANSWER 1 OF 1 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 143:248504 CASREACT

TITLE: Method for producing alkyl lithium compounds and aryl lithium compounds by monitoring the reaction by means of ir-spectroscopy

INVENTOR(S): Weiss, Wilfried; Dawidowski, Dirk; Pleyer, Walter; Krueckel, Frank

PATENT ASSIGNEE(S): Chemetall G.m.b.H., Germany

SOURCE: PCT Int. Appl., 32 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

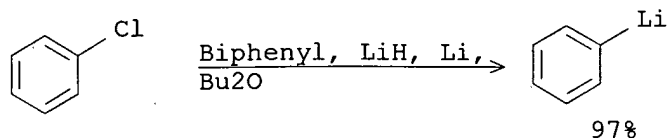
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005082911	A1	20050909	WO 2005-EP1954	20050224
W:				
				AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW
RW:				BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG
DE 102004009445	A1	20050929	DE 2004-10200400944520040227	
EP 1723153	A1	20061122	EP 2005-733858	20050224
R:				AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR
CN 1922192	A	20070228	CN 2005-80005827	20050224
IN 2006CN03106	A	20070608	IN 2006-CN3106	20060825
US 20070152354	A1	20070705	US 2006-589715	20061023
PRIORITY APPLN. INFO.:			DE 2004-10200400944520040227	
			WO 2005-EP1954	20050224

OTHER SOURCE(S): MARPAT 143:248504

AB The invention relates to a method for producing alkyl lithium compds. and aryl lithium compds. by reacting lithium metal with alkyl or aryl halogenides in a solvent, the concentration of the alkyl/aryl halogenide and the alkyl/aryl lithium compound being detected according to an in-line measurement in the reactor by IR spectroscopy, and an exact recognition of the end point of the dosing of the halogenide constituents being carried out by evaluation of the IR measurement. Said method enables an optimum reactive process and reaction yield. The identification of the resp. concentration of the adduct and the product is a reliable reactive process. The yield of the reaction is also optimized by determining the end point of the halogenide dosing, as is the purity of the product due to a lower concentration thereof during the reaction.

RX(5) OF 5



CON: 4 hours, 35 deg C

REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> D L6 IBIB ABS CRD 1-59

L6 ANSWER 1 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 148:144945 CASREACT

TITLE: Remarkable  $\beta$ -Selectivity in the Synthesis of  $\beta$ -1-C-Arylglucosides: Stereoselective Reduction of Acetyl-Protected Methyl 1-C-Aryl-Glucosides without Acetoxy-Group Participation

AUTHOR(S): Deshpande, Prashant P.; Ellsworth, Bruce A.; Buono, Frederic G.; Pullockaran, Annie; Singh, Janak; Kissick, Thomas P.; Huang, Ming-H.; Lobinger, Hildegard; Denzel, Theodor; Mueller, Richard H.

CORPORATE SOURCE: Process Research and Development, Bristol-Myers Squibb, New Brunswick, NJ, 08903, USA

SOURCE: Journal of Organic Chemistry (2007), 72(25), 9746-9749  
CODEN: JOCEAH; ISSN: 0022-3263

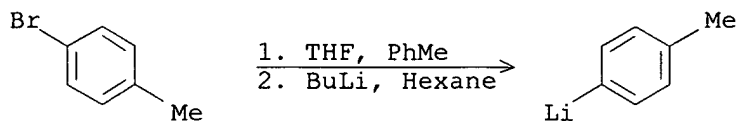
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

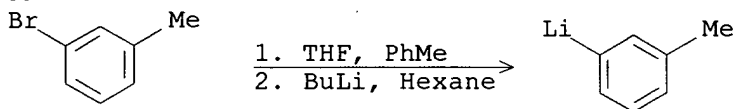
AB An efficient and practical process to generate  $\beta$ -C-aryl-glucoside derivs. was achieved. The process described involves Lewis acid mediated ionic reduction of a peracetylated 1-C-aryl Me glucoside derived from the addition of an aryl-Li to selectively protected  $\delta$ -D-gluconolactone. The reduction of the 2-acetoxy-1-C-oxacarbenium ion intermediates proceeds with a high degree of selectivity to give  $\beta$ -C-aryl-glucosides without 2-acetoxy group participation. Furthermore, during the reduction process we also identified an unprecedented critical role of water. By changing from the usual benzyl ether protecting groups because of cost and chemical compatibility concerns, the new process is made addnl. efficient and highly selective.

RX(3) OF 39



CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

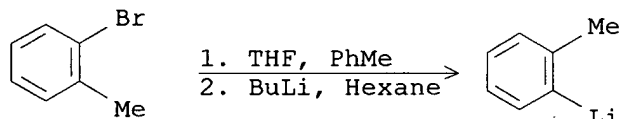
RX(5) OF 39



(step 1)

CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

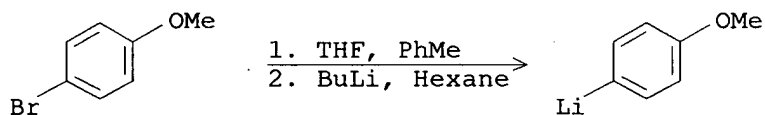
RX(7) OF 39



(step 1)

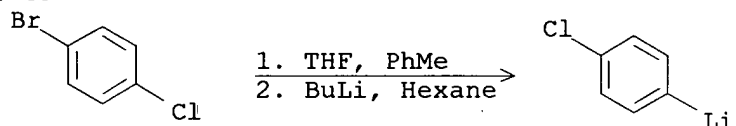
CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(9) OF 39



CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

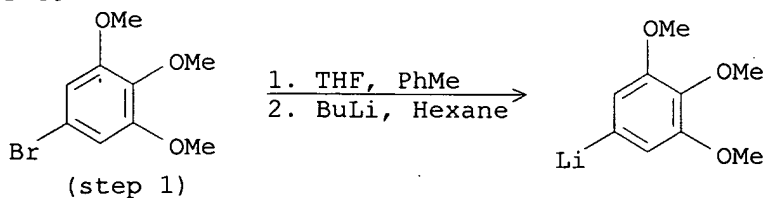
RX(11) OF 39



(step 1)

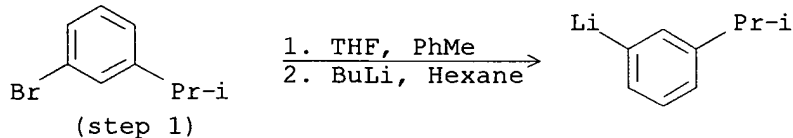
CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(13) OF 39



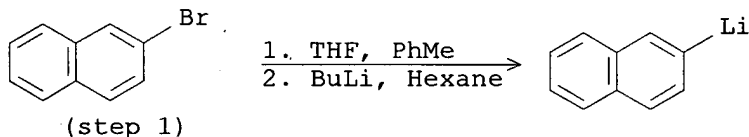
CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(15) OF 39



CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(17) OF 39



CON: STAGE(1) room temperature -> -78 deg C  
STAGE(2) <-65 deg C; 1 hour, -78 deg C

REFERENCE COUNT:

57 THERE ARE 57 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 2 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 147:406167 CASREACT

TITLE: The coupling of butylvinyltellurides with  
organometallic reagents catalyzed by nickel complexes  
AUTHOR(S): Raminelli, Cristiano; Gargalaka, Joao; Silveira,  
Claudio C.; Comasseto, Joao V.

CORPORATE SOURCE: Instituto de Quimica, Universidade de Sao Paulo, Sao  
Paulo, 05508-900, Brazil

SOURCE: Tetrahedron (2007), 63(36), 8801-8809

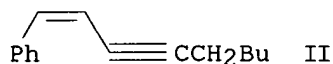
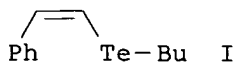
CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Ltd.

DOCUMENT TYPE: Journal

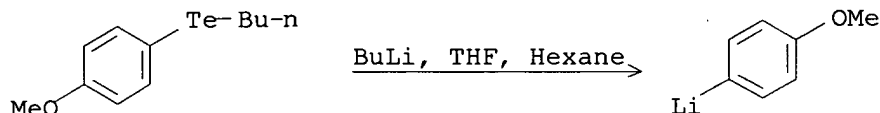
LANGUAGE: English

GI



AB Vinylic tellurides couple efficiently with sp, sp<sup>2</sup> and sp<sup>3</sup> hybridized organometallic compds. (Li, MgX and Zn species) in the presence of dichlorobis(triphenylphosphine)nickel(II) as catalyst. E.g., coupling reaction of (Z)-vinylic telluride I with 1-heptynyllithium, catalyzed by Ni(dppe)Cl<sub>2</sub>, gave 100% (Z)-enyne II.

RX(23) OF 64



CON: 20 minutes, -70 deg C

REFERENCE COUNT: 66 THERE ARE 66 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT.

L6 ANSWER 3 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 144:350731 CASREACT

TITLE: Co-complexes of ortho-dilithiated thiophenol or 2-trimethylsilylthiophenol with lithiated TMEDA molecules: synthesis, crystal structures and theoretical studies (TMEDA = N,N,N',N'-tetramethylethylenediamine)

AUTHOR(S): Hildebrand, Alexandra; Loennecke, Peter; Silaghi-Dumitrescu, Luminita; Silaghi-Dumitrescu, Ioan; Hey-Hawkins, Evamarie

CORPORATE SOURCE: Department of Chemistry, Babes-Bolyai University, Cluj-Napoca, RO-400084, Rom.

SOURCE: Dalton Transactions (2006), (7), 967-974

CODEN: DTARAF; ISSN: 1477-9226

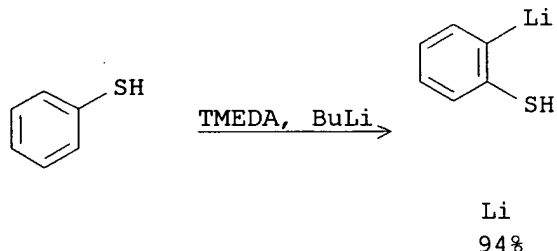
PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

AB When an excess of BuLi was used in the ortho-dilithiation of thiophenol or 2-trimethylsilylthiophenol in the presence of TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine), deprotonation of TMEDA occurred and crystals of [Li<sub>3</sub>{(2-S-C<sub>6</sub>H<sub>4</sub>)(CH<sub>2</sub>MeNCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)(TMEDA)}]<sub>2</sub> (1) or [Li<sub>4</sub>{(2-S-3-SiMe<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)(CH<sub>2</sub>MeNCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>(TMEDA)}] (2) were obtained. MO calcns. on gas-phase 1 and 2 at the DFT B3LYP/6-31G(d) level reproduce the exptl. structures fairly well. In spite of the short Li...cntdot.Li distances, total electron d. representations do not support the existence of Li...cntdot.Li interactions.

RX(4) OF 8



Li  
94%

NOTE: regioselective, standard Schlenk technique used  
CON: 0 deg C -> room temperature

REFERENCE COUNT: 56 THERE ARE 56 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 4 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 142:280267 CASREACT

TITLE: Synthesis and Structural Characterization of Lithium and Trimethyltin Complexes of 2,6-Bis(oxazolinyl)phenyl

AUTHOR(S): Stol, Marianne; Snelders, Dennis J. M.; De Pater, Jeroen J. M.; Van Klink, Gerard P. M.; Kooijman, Huub; Spek, Anthony L.; Van Koten, Gerard

CORPORATE SOURCE: Dutch Polymer Institute and Debye Institute, Department of Metal-Mediated Synthesis, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Utrecht, 3584 CH, Neth.

SOURCE: Organometallics (2005), 24(4), 743-749

CODEN: ORGND7; ISSN: 0276-7333

PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

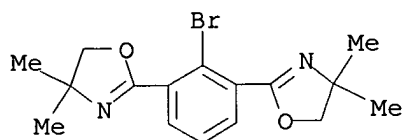
LANGUAGE: English

AB The treatment of 2,6-bis(oxazolinyl)phenyl bromide (Phebox-Br) with BuLi affords a Phebox-Li complex. Subsequent transmetalation with [SnClMe<sub>3</sub>] affords a Phebox-Sn complex. The Phebox ligand can coordinate to a transition metal in various terdentate fashions; both the oxazoline O and the imine N are perfectly positioned for chelation; NCN, OCO, or mixed terdentate coordination modes are theor. possible using this ligand. The structural properties and NMR spectra of [Sn(Me,Me-Phebox)Me<sub>3</sub>] (2) and [Li(R,R'-Phebox)] complexes 3a (R = R' = Me), 3b (R = iPr, R' = H), and 3c (R = tBu, R' = H) were studied. 2 Exhibits no chelation of the Phebox ligand to the Sn center in this case. The [Li(R,R'-Phebox)] complex 3a was crystallog. characterized and is as a mol. dimer (i.e. [Li(Phebox)]<sub>2</sub>), containing two formally three-center-two-electron bonds in a four-membered Li<sub>2</sub>C<sub>2</sub> ring. The formal Phebox anion is bonded to the Li cation via the two ortho imine N centers and the intraannular aromatic C atom. The <sup>13</sup>C{<sup>1</sup>H} NMR signal of Cipso, being a seven-line pattern with coupling constant 1J(<sup>13</sup>C-<sup>7</sup>Li) = 18 Hz, confirms that the dimeric structure is maintained in solution at room temperature. Variable-temperature (VT) NMR studies of 3a indicate that a fluxional

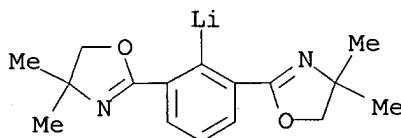
process is occurring at room temperature, which can be frozen out <-16° (ΔG<sub>thermod.</sub> = 56 kJ/mol). This fluxional process is not observed in VT-NMR studies on 3b,c. This is likely due to the presence of bulky (iPr or tBu) substituents that effectively shut down the pathways to rapid inversion of the puckering of the five-membered chelate ring.



RX(5) OF 11



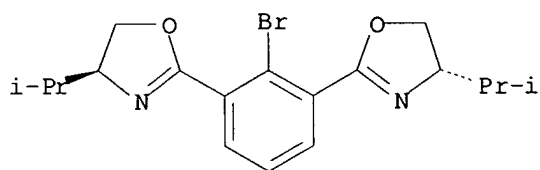
BuLi, Hexane, Pentane →



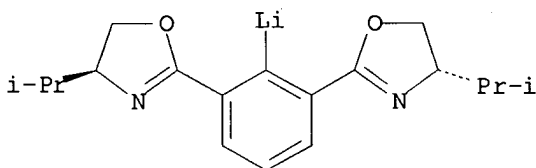
66%

CON: STAGE(1) -78 deg C; -78 deg C → room temperature; 4 hours,  
room temperature

RX(6) OF 11



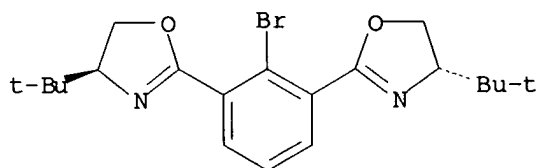
BuLi, Hexane, Pentane →



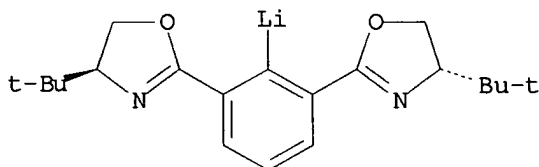
98%

CON: STAGE(1) -78 deg C; -78 deg C → room temperature; 4 hours,  
room temperature

RX(7) OF 11



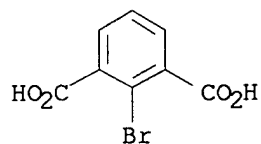
BuLi, Et2O, Hexane →



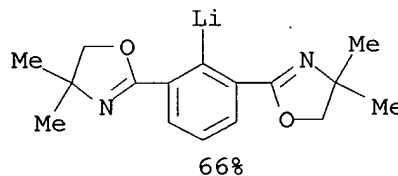
42%

CON: STAGE(1) -78 deg C; 45 minutes, -78 deg C;  
-78 deg C → room temperature; 3 hours, room temperature

RX(9) OF 11 - 2 STEPS



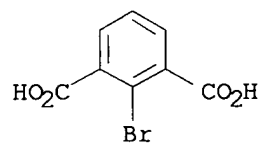
- 1.1. SOCl<sub>2</sub>
- 1.2. HOCH<sub>2</sub>CMe<sub>2</sub>NH<sub>2</sub>,  
Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>
- 1.3. CCl<sub>4</sub>, Et<sub>3</sub>N, PPh<sub>3</sub>,  
MeCN
- 1.4. Water
2. BuLi, Hexane,  
Pentane



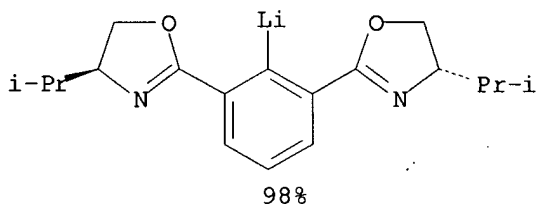
66%

CON: STEP(1.1) overnight, reflux  
 STEP(1.2) 0 deg C; overnight  
 STEP(1.3) 0 deg C; overnight  
 STEP(2.1) -78 deg C; -78 deg C -> room temperature; 4 hours,  
 room temperature

RX(10) OF 11 - 2 STEPS



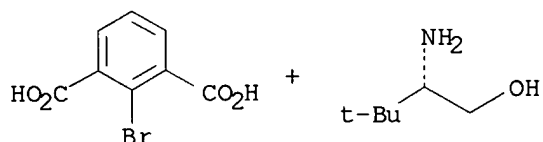
- 1.1. SOCl<sub>2</sub>
- 1.2. (S)-Valinol,  
Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>
- 1.3. CCl<sub>4</sub>, Et<sub>3</sub>N, PPh<sub>3</sub>,  
MeCN
- 1.4. Water
2. BuLi, Hexane,  
Pentane



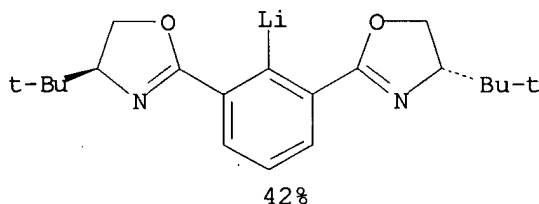
98%

CON: STEP(1.1) overnight, reflux  
 STEP(1.2) 0 deg C; overnight  
 STEP(1.3) 0 deg C; overnight  
 STEP(2.1) -78 deg C; -78 deg C -> room temperature; 4 hours,  
 room temperature

RX(11) OF 11 - 2 STEPS



1.1. SOCl<sub>2</sub>  
1.2. Et<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>  
1.3. CCl<sub>4</sub>, Et<sub>3</sub>N, PPh<sub>3</sub>,  
MeCN  
1.4. Water  
2. BuLi, Et<sub>2</sub>O, Hexane



CON: STEP(1.1) overnight, reflux  
STEP(1.2) 0 deg C; overnight  
STEP(1.3) 0 deg C; overnight  
STEP(2.1) -78 deg C; 45 minutes, -78 deg C;  
-78 deg C -> room temperature; 3 hours, room temperature

REFERENCE COUNT: 43 THERE ARE 43 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 5 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 141:314360 CASREACT

TITLE: Preparation, thermal stability and carbonyl addition reactions of 2,5-difluorophenyl lithium and 2,5-difluorophenyl grignard

AUTHOR(S): Scott, Jeremy P.; Brewer, Sarah E.; Davies, Antony J.; Brands, Karel M. J.

CORPORATE SOURCE: Department of Process Research, Merck Sharp and Dohme Research Laboratories, Hoddesdon, EN11 9BU, UK

SOURCE: Synlett (2004), (9), 1646-1648  
CODEN: SYNLES; ISSN: 0936-5214

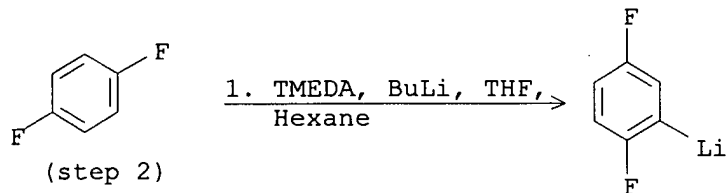
PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

AB The generation of 2,5-difluorophenyl Li 2 by lithiation of 1,4-difluorobenzene with BuLi in THF, with and without amine additives, was surveyed. Thermal stability data of the organolithium species 2 generated with and without TMEDA were determined and the synthetic utility of 2 in the addition to aldehyde and ketone electrophiles is described. Preparation and stability of the corresponding organomagnesium reagent 1, generated by Br-Mg exchange of 1-bromo-2,5-difluorobenzene with isopropylmagnesium chloride, was also examined

RX(2) OF 9



CON: STAGE(1) 10 minutes, <-60 deg C; 10 minutes, -71 deg C  
STAGE(2) 15 minutes, -71 - -68 deg C; 90 minutes,  
-71 - -68 deg C

REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 6 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 137:63283 CASREACT

TITLE: Unusual structures of lithium terphenyl derivatives

AUTHOR(S): Hardman, Ned J.; Twamley, Brendan; Stender, Matthias;  
Baldwin, Richard; Hino, Shirley; Schiemenz, Berthold;  
Kauzlarich, Susan M.; Power, Philip P.

CORPORATE SOURCE: Department of Chemistry, University of California,  
Davis, Davis, CA, 95616, USA

SOURCE: Journal of Organometallic Chemistry (2002), 643-644,  
461-467

CODEN: JORCAI; ISSN: 0022-328X

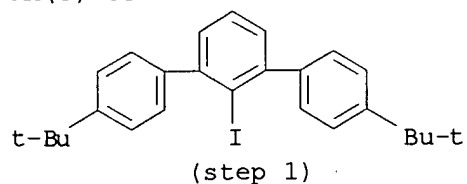
PUBLISHER: Elsevier Science S.A.

DOCUMENT TYPE: Journal

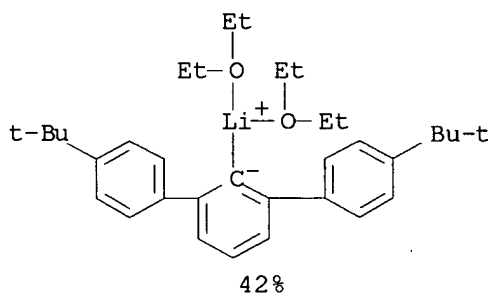
LANGUAGE: English

AB The synthesis, spectroscopic and structural characterization of three new Li derivs. of terphenyl ligands are reported. These are the mixed Li alkyl-Li aryl compound {Li (t-Bu)LiC<sub>6</sub>H<sub>3</sub>-2,6-Trip<sub>2</sub>} (1, Trip = C<sub>6</sub>H<sub>2</sub>-2,4,6-i-Pr<sub>3</sub>), the dilithiated {LiC<sub>6</sub>H<sub>3</sub>-2-(C<sub>6</sub>H<sub>3</sub>-2-Me-5-t-Bu)-6-(C<sub>6</sub>H<sub>3</sub>-2-CH<sub>2</sub>Li-5-t-Bu)·Et<sub>2</sub>O}<sub>2</sub> (2), and the ether solvated (Et<sub>2</sub>O)LiC<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>4</sub>-4-t-Bu)<sub>2</sub> (3). The synthesis of the terphenyl halide precursors for 2 and 3 is also given. The compound 1 resulted from the treatment of 1-IC<sub>6</sub>H<sub>3</sub>-2,6-Trip with two equivalent of Li(t-Bu) in hexane. It features the alkyl and aryl (terphenyl) groups bridged by two Li ions. The Li ions are further solvated by ortho aryl substituents and methyls of the t-Bu groups. This compound is a very rare example of a mixed Li alkyl-Li aryl species. Compound 2 was obtained in low yield from the treatment of 1-BrC<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2-Me-5-t-Bu)<sub>2</sub> with two equivalent of Li(t-Bu). The terphenyl ligand was dilithiated by replacement of the Br and a H from one of the Me groups on the ortho aryl substituents. The ether solvated, dimeric, tetrametallic structure illustrated in the Table of Contents resulted. The compound 3 was obtained from the straightforward lithiation of the iodoterphenyl precursor in the presence of Et<sub>2</sub>O and features a Li ion solvated by two ethers terminally bound to the ipso-C of the terphenyl group.

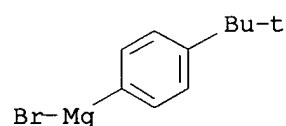
RX(3) OF 7



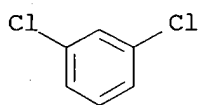
1. BuLi, Hexane  
2. Et<sub>2</sub>O



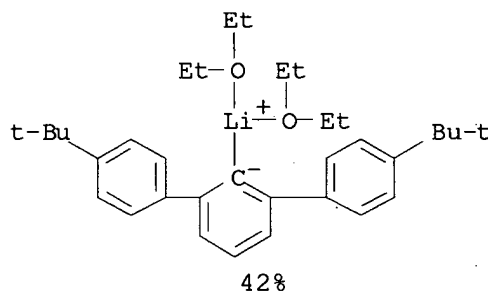
RX(7) OF 7 - 2 STEPS



+



1.1. BuLi, THF, Hexane  
1.2. THF  
1.3. I<sub>2</sub>  
2.1. BuLi, Hexane  
2.2. Et<sub>2</sub>O



REFERENCE COUNT:

21

THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 7 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 127:176492 CASREACT

TITLE: A simple one pot synthesis of 1-chlorophospholes

AUTHOR(S): Teunissen, Herman T.; Hansen, Carola B.; Bickelhaupt, Friedrich

CORPORATE SOURCE: Scheikundig Laboratorium, Vrije Univ., Amsterdam, NL-1081, Neth.

SOURCE: Phosphorus, Sulfur and Silicon and the Related Elements (1996), 118, 309-312  
CODEN: PSSLEC; ISSN: 1042-6507

PUBLISHER: Gordon & Breach

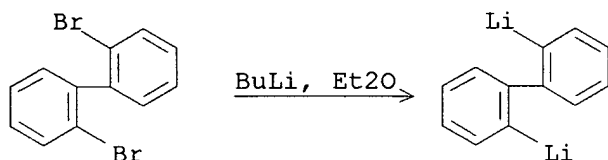
DOCUMENT TYPE: Journal

LANGUAGE: English

AB 1,4-Dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, prepared from diphenylacetylene and Li, was cyclized with PCl<sub>3</sub> to give 57%

1-chloro-2,3,4,5-tetraphenylphosphole. Similarly, 2,2'-dibromobiphenyl gave 77% 5-chlorodibenzo[b,d]phosphole.

RX(2) OF 4



NOTE: 1 H, 20.deg.

REFERENCE COUNT: 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 8 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 127:5187 CASREACT  
 TITLE: Preparation of aryllithium in ether solutions using Lewis bases  
 INVENTOR(S): Schwindeman, James A.; Sutton, Douglas E.; Morrison, Robert C.; Stryker, Sonia S.  
 PATENT ASSIGNEE(S): FMC Corp., USA  
 SOURCE: U.S., 4 pp.  
 CODEN: USXXAM  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5626798	A	19970506	US 1996-587813	19960105
WO 9725334	A1	19970717	WO 1996-US7624	19960524
W: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN				
RW: KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9658036	A	19970801	AU 1996-58036	19960524
DE 19681729	T0	19981217	DE 1996-19681729	19960524
DE 19681729	C2	20001116		

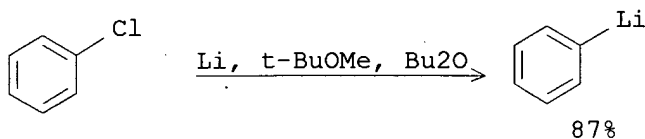
PRIORITY APPLN. INFO.: US 1996-587813 19960105  
 WO 1996-US7624 19960524

OTHER SOURCE(S): MARPAT 127:5187

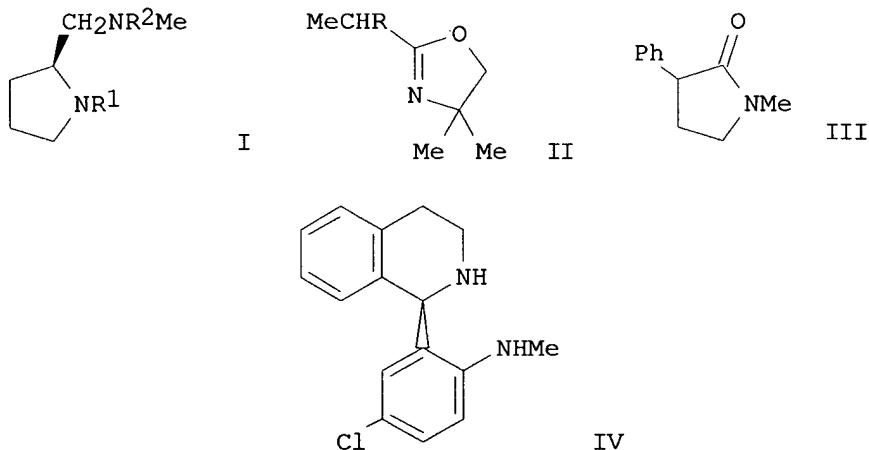
AB An improved process for producing high purity solns. of aryllithium compds. and the product solns. are claimed. The process comprises reacting a particulate alkali metal having a particle size of 10-300 µm, with an aryl halide in a normally liquid ethereal solvent ROR<sub>1</sub>, wherein R and R<sub>1</sub> are selected from the group of alkyl radicals containing from 3 to 6 C atoms, in the presence of a Lewis base selected from compds. of the formula: R<sub>2</sub>AR<sub>3</sub>(R<sub>4</sub>)<sub>z</sub> and cyclic -(CR<sub>5</sub>R<sub>6</sub>)<sub>y</sub>-(A(R<sub>4</sub>)<sub>z</sub>)- wherein A is selected from O, N, P or S; R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are selected from alkyl radicals containing from 1 to 6 C atoms; R<sub>5</sub> and R<sub>6</sub> are independently selected from H or alkyl radicals containing one to six C atoms; y = 4 to 6; but when A is O or S, z = 0; and when A is N or P, z = 1, and provided there is a mole ratio of ether to aryl halide of at least 1.3 to 1 and a mole ratio of Lewis base to aryl halide of from 0.01 to 0.5. For example, to a reaction flask containing 1.25 mol Li powder and 0.94 mol Bu<sub>2</sub>O was added, dropwise, over a period of 60 min, a solution of 0.52 mol PhCl and

0.052 mol MeOtBu, while maintaining the reaction temperature at 30-35°; the yield of PhLi was 87.4%. If no MeOtBu was present, the yield was 80.8% and the reaction was slower (16% PhCl remaining after 120 min vs. 6%).

RX(1) OF 1



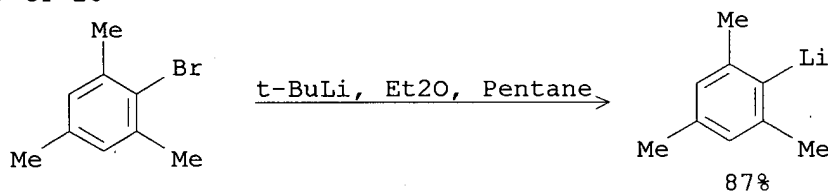
L6 ANSWER 9 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 123:284845 CASREACT  
 TITLE: Lewis Acid-Induced Internal Proton Return in Enolate Complexes with Chiral Amines  
 AUTHOR(S): Vedejs, Edwin; Lee, Namkyu  
 CORPORATE SOURCE: Chemistry Department, University of Wisconsin, Madison, WI, 53706, USA  
 SOURCE: Journal of the American Chemical Society (1995), 117(3), 891-900  
 CODEN: JACSAT; ISSN: 0002-7863  
 PUBLISHER: American Chemical Society  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI



AB Treatment of a 1:1:1 mixture of enolate  $\text{RCMe:C(OLi)N(CHMe}_2)_2$  ( $\text{R} = 6\text{-methoxy-2-naphthyl}$ ) (5), amine I [ $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{CH}_2\text{CH}_2\text{NMe}_2$ ], and lithium amide I ( $\text{R}_1 = \text{Li}$ ,  $\text{R}_2 = \text{CH}_2\text{CH}_2\text{NMe}_2$ ) with  $\text{BF}_3 \cdot \text{OEt}_2$  affords the naproxen amide  $\text{RCHMeCON(CHMe}_2)_2$  (4a; same R) with an enantiomer excess of 77% (>90% yield). The result is attributed to Lewis acid-induced internal proton return (ipr) in a mixed aggregate containing the enolate and the chiral amine. Use of proline-derived diamines I ( $\text{R}_1 = \text{H}$ ,  $\text{R}_2 = \text{Me}$ , Ph) in place of 6 affords 4a with 56-66% ee, but monoamines are relatively ineffective. Similar ipr conditions can be used to deracemize the oxazolidine II (same R) (50-60%), the lactam III (50% ee), and N,N-diisopropyl-2-(1-cyclohexenyl)propionamide (62% ee). However,

disappointing results were obtained with several esters and  $\alpha$ -(2-naphthyl)- $\gamma,\gamma$ -dimethyl- $\gamma$ -valerolactone (18). Lactone 18 was deracemized with the diamine IV (70% ee) under ipr conditions, but simple acyclic esters gave marginal ee values with IV ( $\text{BF}_3 \cdot \text{OEt}_2$  quench). Better results were obtained with Me N-benzoylalaninate (73% ee). In the latter case, the dianion was generated and ipr was induced by the sequential addition of IV and  $\text{BF}_3 \cdot \text{OEt}_2$  as before. In the case of amide 4a,  $^1\text{H}$  NMR evidence shows that much of the proton transfer is complete before the addition of  $\text{BF}_3 \cdot \text{OEt}_2$  to the solution of IV and enolate 5. Thus, 5 is quenched by direct proton transfer, not by ipr, when 24 is used as the chiral amine. The proton transfer pathway can be correlated qual. with  $\text{pK}_a$  DMSO values. Thus, 24 was found to have a  $\text{pK}_a$  DMSO = 27.7 while the value for 4a is ca. 31. The relative acidity in THF is assumed to be similar, and 24 can protonate 5 directly but not the lactone enolate (18:  $\text{pK}_a$  (DMSO) = 20.1). Direct proton transfer does not occur with 6 (estimated  $\text{pK}_a$  DMSO = ca. 34-35) with any of the enolates studied and activation for ipr by  $\text{BF}_3 \cdot \text{OEt}_2$  is necessary to activate the N-H bond. In several examples, protic acid-induced ipr was also explored. In all cases, this gave lower ee values than the  $\text{BF}_3 \cdot \text{OEt}_2$  method.

RX(11) OF 28



L6 ANSWER 10 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

123:228304 CASREACT

TITLE:

An efficient procedure for the synthesis of C-chiral bisphosphines

AUTHOR(S):

McKinstry, Lydia; Livinghouse, Tom

CORPORATE SOURCE:

Dep. Chem. Biochem., Montana State Univ., Bozeman, MT, 59717, USA

SOURCE:

Tetrahedron (1995), 51(28), 7655-66

CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER:

Pergamon

DOCUMENT TYPE:

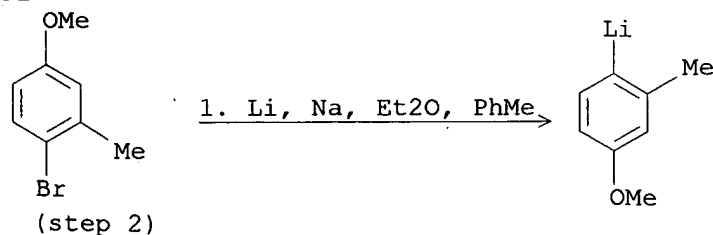
Journal

LANGUAGE:

English

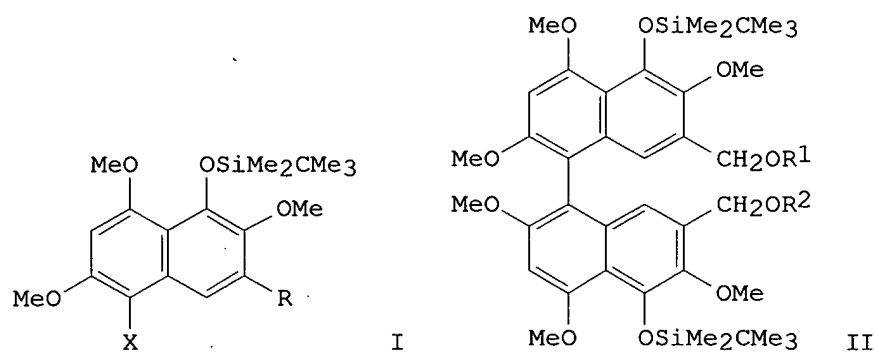
AB A practical method for the synthesis of bisphosphines containing homochiral C backbones, e.g., (2R,4R)-2,4-bis(dicyclohexylphosphino)pentane, is described. This procedure entails sequential reaction of a homochiral ditosylate, e.g., (2S,4S)-2,4-pentanediol di-p-toluenesulfonate, with the appropriate dialkyl- or diarylphosphine-borane anion, e.g.,  $\text{R}_2\text{P} \cdot \text{BH}_3^- \text{Li}^+$  (e.g., R = cyclohexyl, Ph) followed by  $\text{BH}_3$  decomplexation mediated by  $\text{HBF}_4 \cdot \text{OMe}_2$ .

RX(4) OF 92



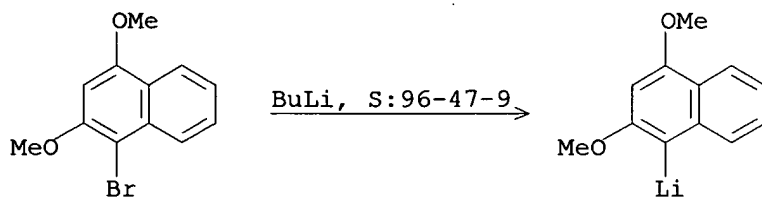


L6 ANSWER 11 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 119:49043 CASREACT  
 TITLE: Application of a copper(I)-mediated biaryl cross-coupling reaction to the synthesis of oxygenated 1,1'-binaphthalenes  
 AUTHOR(S): Coleman, Robert S.; Grant, Eugene B.  
 CORPORATE SOURCE: Dep. Chem. Biochem., Univ. South Carolina, Columbia, SC, 29208, USA  
 SOURCE: Tetrahedron Letters (1993), 34(14), 2225-8  
 CODEN: TELEAY; ISSN: 0040-4039  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI

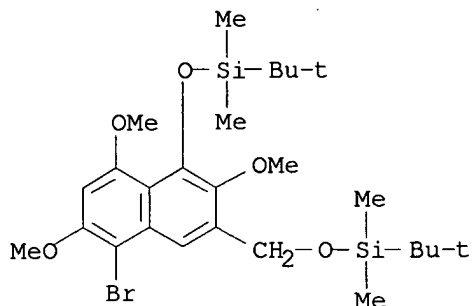


AB Application of an oxidative copper(I)-mediated biaryl cross-coupling protocol to the synthesis of highly oxygenated, differentially substituted 1,1'-binaphthalenes related to the perylenequinone calphostin C is detailed. Thus, coupling of naphthalene I (R = CH<sub>2</sub>OR<sub>1</sub>, R<sub>1</sub> = SiMe<sub>2</sub>CMe<sub>3</sub>, X = Li) with I (R = CH<sub>2</sub>OR<sub>2</sub>, R<sub>2</sub> = SiPh<sub>2</sub>CMe<sub>3</sub>, X = CuCNLi) gave binaphthalene II.

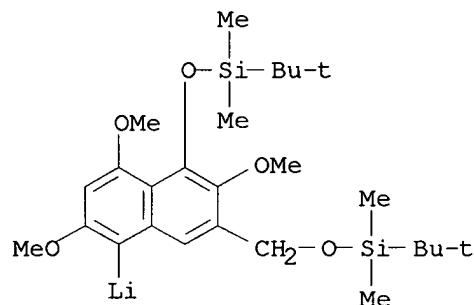
RX(1) OF 21



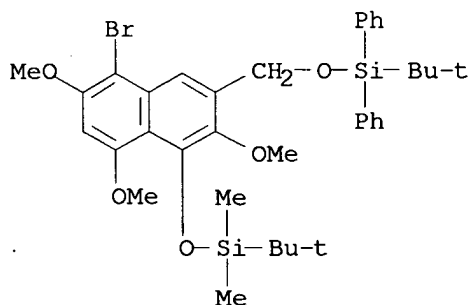
RX(5) OF 21



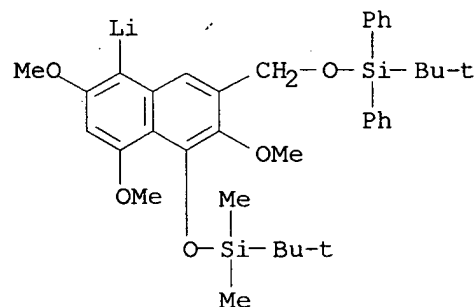
BuLi, S:96-47-9



RX(6) OF 21



BuLi, S:96-47-9



L6 ANSWER 12 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 118:102236 CASREACT  
TITLE: Preparation of aryllithiums in C6 dialkyl ether solvents  
INVENTOR(S): Morrison, Robert Charles  
PATENT ASSIGNEE(S): FMC Corp., USA

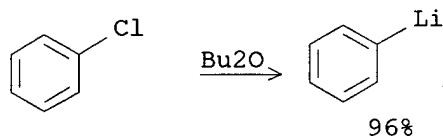
SOURCE: PCT Int. Appl., 21 pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9219622	A1	19921112	WO 1992-US1208	19920214
W: AU, BB, BG, BR, CA, CS, FI, HU, JP, KP, KR, LK, MG, MW, NO, RO, RU, SD				
RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FR, GA, GB, GN, GR, IT, LU, MC, ML, MR, NL, SE, SN, TD, TG				
AU 9219262	A	19921221	AU 1992-19262	19920214
PRIORITY APPLN. INFO.:			US 1991-692438	19910429
			WO 1992-US1208	19920214

OTHER SOURCE(S): MARPAT 118:102236

AB Thermally stable solns. of aryllithium compds. were prepared by reaction of Li dispersions with monohaloaryl compds. in solvents ROR1 (R, R1 = C3-8 alkyl; ≥6 carbons total) with a molar ratio of ether/monohaloaryl compound of ≥1.5 at a temperature of 5-65°. Thus, 1 equiv PhCl was added dropwise to a stirred slurry of Li in 1.8 equiv BuOBu followed by a postreaction period and filtration to give a .apprx.25% solution of PhLi which was stable for ≥40 days at 20-22°.

RX(1) OF 1



NOTE: product has improved stability in this solvent

L6 ANSWER 13 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 117:212546 CASREACT

TITLE: Dependence of the ability of 2-substituted thiophenes to inhibit reactions of organic halides with lithium on the electronic properties of substituents. Direct lithiation of 2-methylthiophene by butyl chloride and Li in ethyl ether

AUTHOR(S): Koikov, L. N.; Polikarpov, M. V.; Alekseeva, N. V.; Lisitsa, E. A.

CORPORATE SOURCE: Vses. Nauchno-Issled. Inst. im. Ordzhonikidze, Moscow, Russia

SOURCE: Metalloorganicheskaya Khimiya (1992), 5(3), 590-3  
 CODEN: MEKHEX; ISSN: 0235-0114

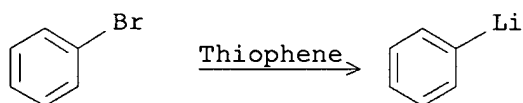
DOCUMENT TYPE: Journal

LANGUAGE: Russian

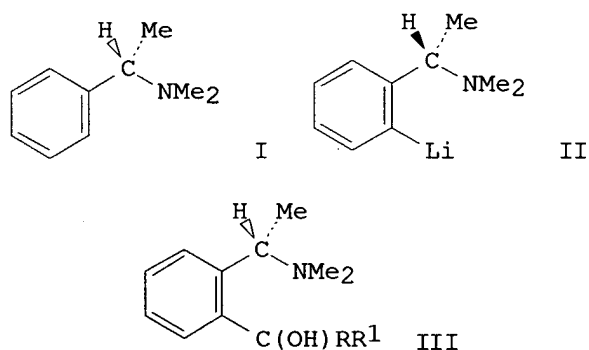
AB 2-Chloro- and 2-bromothiophene and selenophene inhibit the reaction of PhBr with Li in Et2O similar to thiophene, while 2-methyl-, 2,5-dimethyl-, and 2,5-dichlorothiophene do not. In contrast to BuSH, PhCH2SH, which gives an ether-soluble Li thiolate, is not an inhibitor. Formation of an unstable radical anion from a d-heterocycle that decomp. into an Et2O-insol. Li thiolate or chalcogenide is presumed necessary for displaying the inhibiting properties. The difference in behavior of thiophene with donor (Me) and acceptor (Cl, Br) substituents, which have close steric characteristics, is accounted for by the inability of the former to give a radical anion. On the basis of the

data obtained, a preparative one-stage synthesis of 5-methyl-2-thienyllithium was developed from BuCl and Li in Et<sub>2</sub>O. Subsequent carboxylation leads to 5-methyl-2-thiophenecarboxylic acid in 74% yield.

RX(1) OF 1

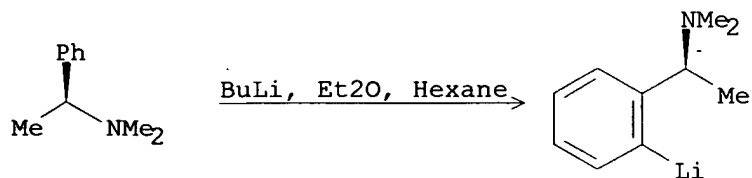


L6 ANSWER 14 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 117:69500 CASREACT  
 TITLE: Lithiation of (S)-(-)-N,N-dimethyl-1-phenylethylamine  
 AUTHOR(S): Dem'yanovich, V. M.; Shishkina, I. N.; Vedernikov, A. I.  
 CORPORATE SOURCE: Mosk. Gos. Univ., Moscow, Russia  
 SOURCE: Zhurnal Organicheskoi Khimii (1991), 27(12), 2628-9  
 CODEN: ZORKAE; ISSN: 0514-7492  
 DOCUMENT TYPE: Journal  
 LANGUAGE: Russian  
 GI



AB Lithiation of benzylamine (S)-(-)-I by BuLi in Et<sub>2</sub>O or hexane takes place only at the ortho position to give Li derivative II. Reaction of II with RR<sup>1</sup>CO [R = R<sup>1</sup> = Ph, Me; R = H, R<sup>1</sup> = Ph; RR<sup>1</sup> = (CH<sub>2</sub>)<sub>5</sub>] gave 30-87% amino alcs. III.

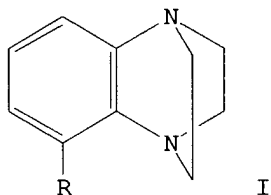
RX(1) OF 3



NOTE: Regioselective, either solvent

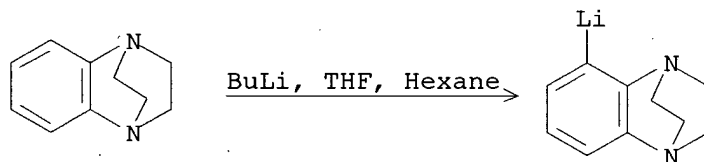
L6 ANSWER 15 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 116:21017 CASREACT  
 TITLE: Diazabicycloalkanes with nitrogen atoms in bridgehead positions. 21. Heteroatom-promoted lithiation of benzo[b]-1,4-diazabicyclo[2.2.2]octene and introduction of substituents into the annelating benzene ring  
 AUTHOR(S): Gall, A. A.; Trachum, A. S.; Romantsev, V. A.; Shishkin, G. V.  
 CORPORATE SOURCE: Novosib. Inst. Bioorg. Khim., Novosibirsk, 630090, USSR  
 SOURCE: Khimiya Geterotsiklicheskikh Soedinenii (1991), (6), 798-803  
 CODEN: KGSSAQ; ISSN: 0453-8234  
 DOCUMENT TYPE: Journal  
 LANGUAGE: Russian  
 GI



AB The lithiation of the title compound I (R = H) gave I (R = Li), the reaction of which with a no of electrophiles afforded derivs. I [R = Br, I, CO<sub>2</sub>H, OH, SiMe<sub>3</sub>, B(OH)<sub>3</sub>, CHO, 1-hexylthio].

RX(1) OF 5

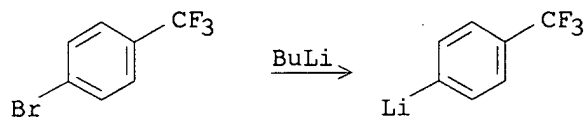


L6 ANSWER 16 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 113:211557 CASREACT  
 TITLE: Preparation of  $\alpha$ -[4-(trifluoromethyl)phenyl]benzenemethanols  
 INVENTOR(S): Davidson, James G., III; Swierenga, Brian S.  
 PATENT ASSIGNEE(S): Warner-Lambert Co., USA  
 SOURCE: U.S., 6 pp.  
 CODEN: USXXAM  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4940822	A	19900710	US 1988-267428	19881104
PRIORITY APPLN. INFO.:			US 1988-267428	19881104
OTHER SOURCE(S): MARPAT 113:211557				
AB 4-(F <sub>3</sub> C)C <sub>6</sub> H <sub>4</sub> CH(OR)C <sub>6</sub> H <sub>4</sub> R <sub>1</sub> (R = Li, H; R <sub>1</sub> = H, halo, (halo)alkyl, aryl, etc.) are prepared by combining 4-(F <sub>3</sub> C)C <sub>6</sub> H <sub>4</sub> Br and BuLi reagent streams				

in a flow-through reactor the output of which is combined with a reagent stream comprising  $\text{R1C6H4CHO}$  in a second flow-through reactor the output of which is received in a reactor containing an acid salt or mineral acid.

RX(1) OF 1



L6 ANSWER 17 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 112:98685 CASREACT

TITLE: Synthesis and pyrolysis of organoelement benzazole derivatives of phosphorus, arsenic, silicon and tin

AUTHOR(S): Heinicke, Joachim

CORPORATE SOURCE: Sekt. Chem., Martin-Luther-Univ., Halle-Wittenberg, Halle/Saale, 4010, Ger. Dem. Rep.

SOURCE: Journal of Organometallic Chemistry (1989), 364(3), C17-C21

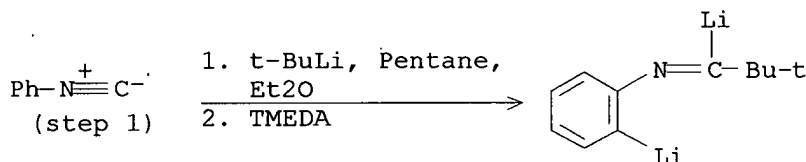
CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

LANGUAGE: German

AB 3-Organ-1,3-benzazaphospholes and -benzazarsoles as well as 3,3-disubstituted 1,3-benzazasiloles and -benzazastannoles are prepared from  $\text{o-LiC6H6N:C(Li)CMe3}$  and the relevant organoelement dichlorides. The heterocycles obtained are converted by flash vacuum pyrolysis into the aromatic 1H-1,3-benzazaphospholes and benzazaarsoles, resp.

RX(1) OF 23



NOTE: thermal

L6 ANSWER 18 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 112:77266 CASREACT

TITLE: Isolation and crystal structure of a presumed intermediate in the reaction of an organolithium compound with an epoxide

AUTHOR(S): Harder, Sjoerd; Boersma, Jaap; Brandsma, Lambert; Kanters, Jan A.; Duisenberg, Albert J. M.; Van Lenthe, Joop H.

CORPORATE SOURCE: Dep. Met.-Mediated Synth., Univ. Utrecht, Utrecht, 3584, Neth.

SOURCE: Organometallics (1990), 9(2), 511-16  
CODEN: ORGND7; ISSN: 0276-7333

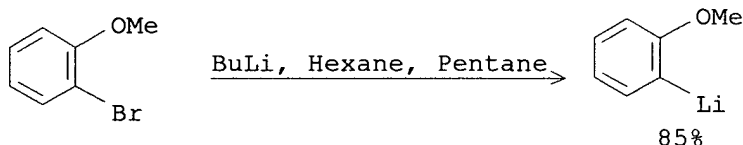
DOCUMENT TYPE: Journal

LANGUAGE: English

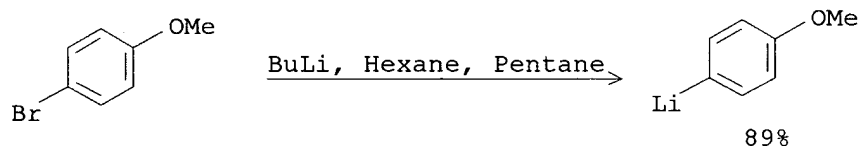
AB The organolithium-epoxide complexes tetrakis(1-lithio-2-methoxybenzene)bis(ethylene oxide) and tetrakis(1-lithio-2-methoxybenzene)bis(propylene oxide), which are thought to be intermediates in the  $\beta$ -hydroxyalkylation of organolithium compds., have been

isolated and characterized. NMR studies on these complexes in nonpolar solvents such as C<sub>6</sub>H<sub>6</sub> and PhMe provide evidence for epoxide O to Li coordination. Addnl., the propylene oxide complex has been characterized by single-crystal x-ray diffraction at 100 K. The structure consists of a tetrameric aggregate of 1-lithio-2-methoxybenzene and two disordered propylene oxide mols., which coordinate to Li as external Lewis bases. Since ab initio calcns. (RHF; SV 3-21G) show the activation of the epoxide by Li coordination to be very small, the question of whether such complexes are intermediates in the nucleophilic ring opening of epoxides remains unanswered.

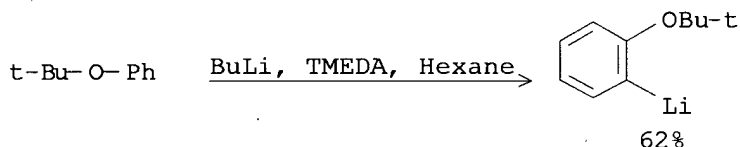
RX(1) OF 7



RX(2) OF 7



RX(3) OF 7



L6 ANSWER 19 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 110:135377 CASREACT

TITLE: 2-Phosphino- and 2-phosphinylbenzenethiols: new ligand types

AUTHOR(S): Block, Eric; Ofori-Okai, Gabriel; Zubieta, Jon

CORPORATE SOURCE: Dep. Chem., State Univ. New York, Albany, NY, 12222, USA

SOURCE: Journal of the American Chemical Society (1989), 111(6), 2327-9

CODEN: JACSAT; ISSN: 0002-7863

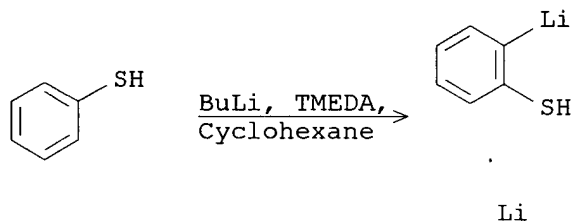
DOCUMENT TYPE: Journal

LANGUAGE: English

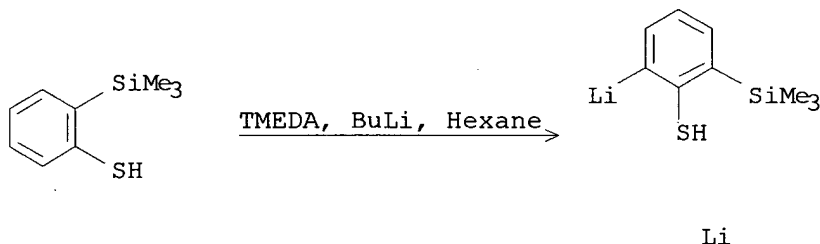
AB Treatment of 2-LiC<sub>6</sub>H<sub>4</sub>SLi with Ph<sub>2</sub>PCl, PhPCl<sub>2</sub>, PCl<sub>3</sub>, Ph<sub>2</sub>P(O)Cl, PhP(O)Cl<sub>2</sub>, and POCl<sub>3</sub> gives, resp., 2-(diphenylphosphino)benzenethiol, bis(2-mercaptophenyl)phenylphosphine, tris(2-mercaptophenyl)phosphine, 2-(diphenylphosphinyl)benzenethiol, bis(2-mercaptophenyl)phenylphosphine oxide (I), and tris(2-mercaptophenyl)phosphine oxide. Treatment of Li 2-lithio-6-trimethylsilylbenzenethiolate with Ph<sub>2</sub>PCl, PhPCl<sub>2</sub>, PCl<sub>3</sub>, Ph<sub>2</sub>P(O)Cl, PhP(O)Cl<sub>2</sub>, and POCl<sub>3</sub> gives, resp., 2-(diphenylphosphino)-6-trimethylsilylbenzenethiol, bis[2-mercapto-6-(trimethylsilyl)phenyl]phenylphosphine, tris[2-mercapto-6-(trimethylsilyl)phenyl]phosphine, 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol, bis[2-mercapto-6-(trimethylsilyl)phenyl]phenylphosphine oxide, and tris[2-mercapto-6-(trimethylsilyl)phenyl]phosphine oxide. Interesting trends seen in the

<sup>31</sup>P NMR spectra of compds. are discussed. Oxidation of I with DMSO affords 11-phenyl-11H-dibenzo[c,f][1,2,5]dithiaphosphepin 11-oxide, a new heterocyclic ring system. Compds. prepared may be useful as ligands for transition metals.

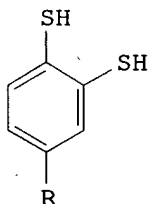
RX(3) OF 30



RX(4) OF 30



L6 ANSWER 20 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 110:57733 CASREACT  
 TITLE: o-Lithiothiophenol equivalents. Generation, reactions and applications in synthesis of hindered thiolate ligands  
 AUTHOR(S): Block, Eric; Eswarakrishnan, Venkatachalam; Gernon, Michael; Ofori-Okai, Gabriel; Saha, Chantu; Tang, Kaluo; Zubieta, Jon  
 CORPORATE SOURCE: Dep. Chem., State Univ. New York, Albany, NY, 12222, USA  
 SOURCE: Journal of the American Chemical Society (1989), 111(2), 658-65  
 CODEN: JACSAT; ISSN: 0002-7863  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI

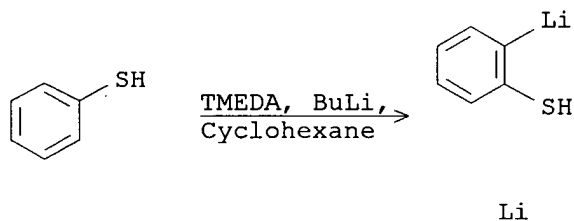


AB Treatment of 2-(phenylthio)tetrahydropyran with Me<sub>3</sub>CLi in THF-HMPA at -90° followed by Me<sub>3</sub>SiCl or Et<sub>3</sub>SiCl and then HgCl<sub>2</sub>-H<sub>2</sub>S affords 2-(trimethylsilyl)benzenethiol (I) or 2-(triethylsilyl)benzenethiol (II), resp. I and II can also be obtained directly from thiophenol by conversion of the latter to Li 2-lithiobenzenethiolate (III)

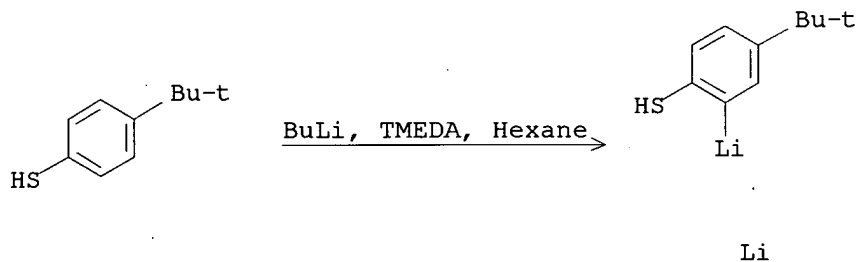


followed by quenching of a THF solution of III at  $-78^{\circ}$  with an equivalent of the appropriate chlorosilane; by this same procedure, 4-tert-butylbenzenethiol can be converted into 4-tert-butyl-2-(trimethylsilyl)benzenethiol via Li 4-tert-butyl-2-lithiobenzenethiolate (IV) and 2-naphthalenethiol can be transformed into 3-(trimethylsilyl)-2-naphthalenethiol via lithium 3-lithio-2-naphthalenethiolate. Reaction of I with BuLi in hexane followed by Me<sub>3</sub>SiCl gives 2,6-bis(trimethylsilyl)benzenethiol together with products derived from lithiation of the silyl Me groups. Treatment of III in THF with Me<sub>2</sub>SiCl<sub>2</sub> and ClMe<sub>2</sub>SiSiMe<sub>2</sub>Cl affords bis(2-mercaptophenyl)dimethylsilane (V) and 1,2-bis(2-mercaptophenyl)tetramethyldisilane, resp. Oxidation of V yields 5,5-dimethyldibenzo[b,e]-5-sila-1,2-dithiepin. Treatment of IV with Et<sub>2</sub>SiCl<sub>2</sub> and Ph<sub>2</sub>SiCl<sub>2</sub> affords bis(4-tert-butyl-2-mercaptophenyl)diethylsilane and bis(4-tert-butyl-2-mercaptophenyl)diphenylsilane, resp. Thiophenol can be transformed into 1,2-benzenedithiol VI (R = H); similarly 4-tert-butylbenzenethiol can be converted into 4-tert-butyl-1,2-benzenedithiol VI (R = Me<sub>3</sub>C). Compound VI (R = H) can be further transformed into 1,2,3-benzenetrithiol. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of dilithio salts III and IV were determined

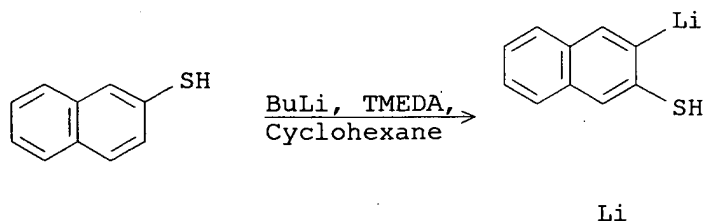
RX(9) OF 73



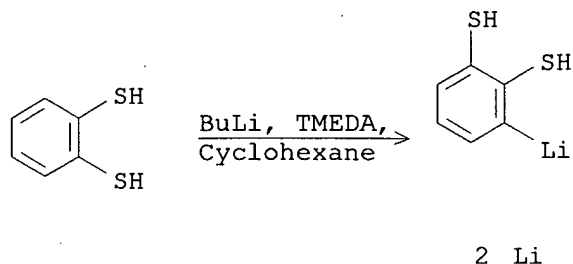
RX(12) OF 73



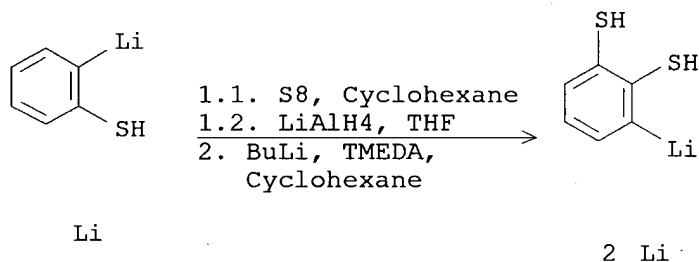
RX(23) OF 73



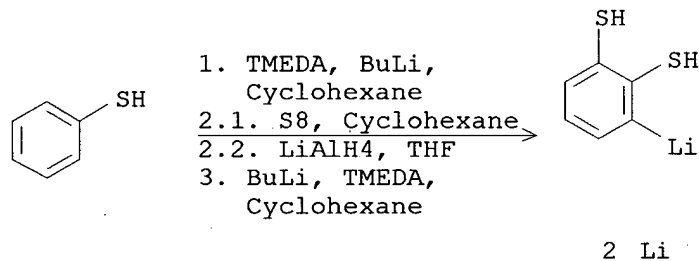
RX(26) OF 73



RX(55) OF 73 - 2 STEPS



RX(66) OF 73 - 3 STEPS



L6 ANSWER 21 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

109:37892 CASREACT

TITLE:

Organophosphorus intermediates. IX. The cleavage of  $\alpha$ ,  $\omega$ -bis(diphenylphosphino)alkanes with lithium. A phosphorus-31 NMR study

AUTHOR(S):

Brooks, Peter; Gallagher, Michael J.; Sarroff, Adrian Sch. Chem., Univ. New South Wales, Kensington, 2033, Australia

CORPORATE SOURCE:

SOURCE:

Australian Journal of Chemistry (1987), 40(8), 1341-51  
CODEN: AJCHAS; ISSN: 0004-9425

DOCUMENT TYPE:

Journal

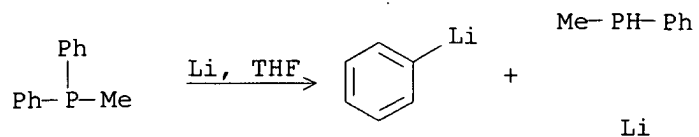
LANGUAGE:

English

AB

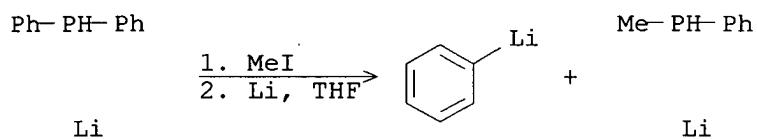
The title phosphines,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 2-5$ ), reacts with Li in THF to give the corresponding 1,n-dilithio-1,n-di(phenylphosphines) directly with little or no intermediacy of the 1-lithio-1-phenyl-n-diphenylphosphinoalkanes which can, however, be obtained by arylation of the diphosphides. Methylenebis(diphenylphosphine) and 1,4-diphenyl-1,4-diphosphinate undergo exclusive P-alkyl C cleavage. The chemical and  $^{31}\text{P}$  NMR spectroscopy of the diphosphides are described and the mechanism of the cleavage reaction is discussed. Some cleavage reactions in liquid ammonia are described.

RX(10) OF 47



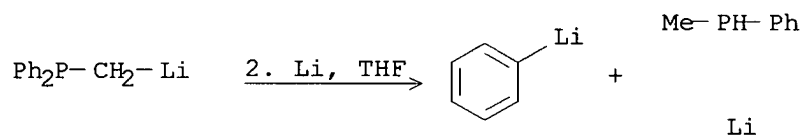
NOTE: Sonication

RX(29) OF 47 - 2 STEPS



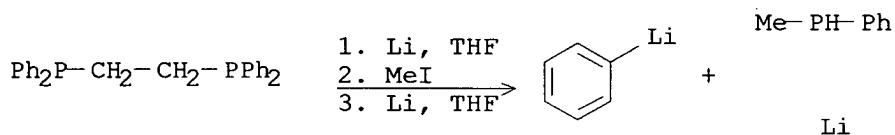
NOTE: 2) Sonication

RX(30) OF 47 - 2 STEPS



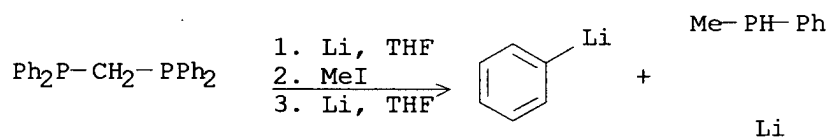
NOTE: 2) Sonication

RX(35) OF 47 - 3 STEPS



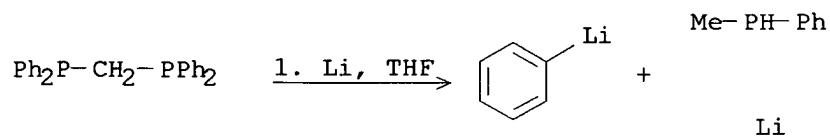
NOTE: 1) Sonication, 3) Sonication

RX(36) OF 47 - 3 STEPS



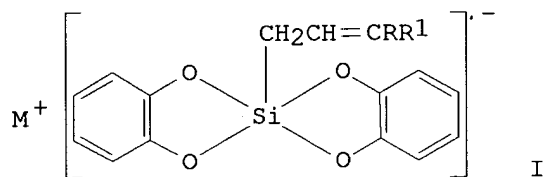
NOTE: 1) Sonication, 3) Sonication

RX(37) OF 47 - 3 STEPS



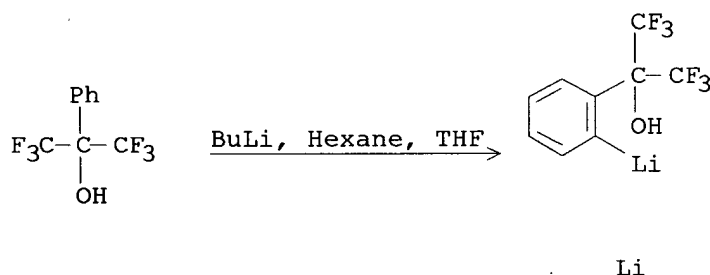
NOTE: 1) Sonication, 3) Sonication

L6 ANSWER 22 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 109:23020 CASREACT  
 TITLE: Chemistry of organosilicon compounds. 240.  
 Pentacoordinate allylsilicates: characterization and highly stereoselective reaction with aldehydes  
 AUTHOR(S): Kira, Mitsuo; Sato, Kazuhiko; Sakurai, Hideki  
 CORPORATE SOURCE: Fac. Sci., Tohoku Univ., Sendai, 980, Japan  
 SOURCE: Journal of the American Chemical Society (1988), 110(14), 4599-602  
 CODEN: JACSAT; ISSN: 0002-7863  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI



AB Lithium and bis(triphenylphosphoranylidene)ammonium salts of bis(1,2-benzenediolato)allylsilicates, i.e., I [R,R1 = H, Me; M = Li, (Ph3P)2N] which were prepared by reaction of allyl-, phenyl-, and (E)- and (Z)-crotyltrichlorosilanes with dilithium catecholate, reacted with PhCHO or furfural to give the corresponding homoallyl alcs. in a regiospecific and highly diastereoselective manner in 80-90% yields. A six-membered cyclic transition state, which is favored by the enhanced nucleophilicity of the  $\gamma$ -carbon of the allylsilicates as well as by the significant Lewis acidity giving hexacoordinate silicates, is proposed. However, allylsilicates with  $\alpha,\alpha$ -bis(trifluoromethyl)benzenemethanolato(2-)-C2,O ligands did not react with the aldehydes.

RX(17) OF 50



L6 ANSWER 23 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 108:131983 CASREACT  
 TITLE: Reactions of MCl5 (M = niobium or tantalum) with excess phenyllithium: structural characterization of bisbenzyne/polyphenyl derivatives of niobium and tantalum  
 AUTHOR(S): Bartlett, Ruth A.; Power, Philip P.; Shoner, Steven C.  
 CORPORATE SOURCE: Dep. Chem., Univ. California, Davis, CA, 95616, USA  
 SOURCE: Journal of the American Chemical Society (1988),

DOCUMENT TYPE:

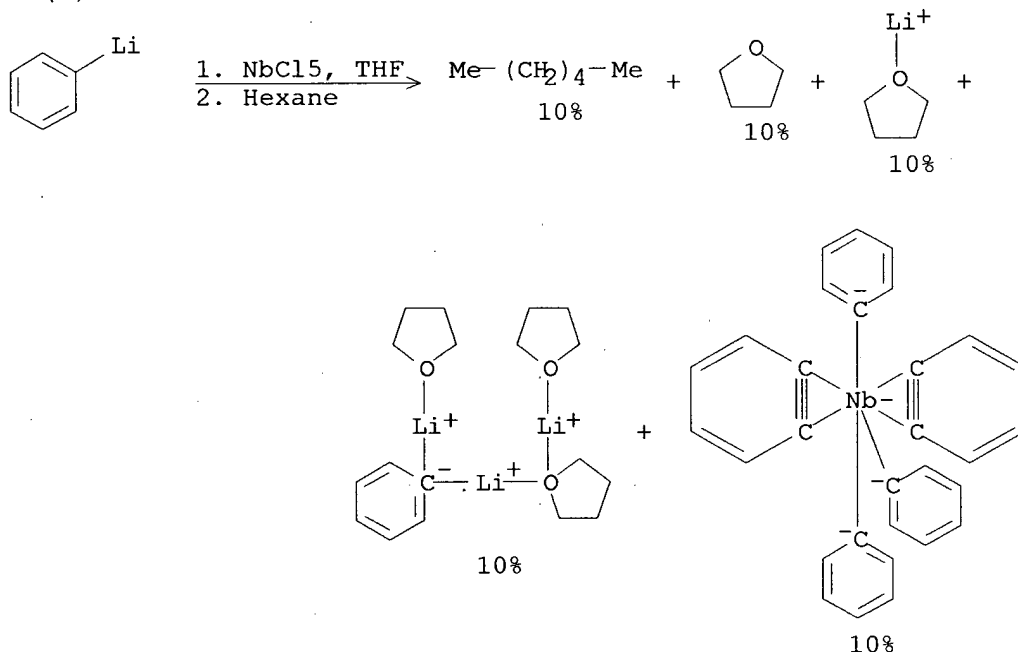
Journal

LANGUAGE:

English

AB The complexes  $[\text{Nb}(\eta^2\text{-C}_6\text{H}_4)_2\text{Ph}_3(\text{LiPh}\cdot\text{THF})(\text{LiTHF})_4]\cdot 0.5\text{THF}\cdot 0.5\text{ n-C}_6\text{H}_{14}$  (I) and  $[\text{Ta}(\eta^2\text{-C}_6\text{H}_4)_2\text{Ph}_4(\text{LiTHF})_2]_2[\text{Li}_4\text{Cl}_2(\text{THF})_10]$  were prepared from  $\text{MCl}_5$  ( $\text{M} = \text{Nb}, \text{Ta}$ ) and  $\text{PhLi}$ . They are the first examples of mononuclear bisbenzyne derivs. and appear to be stabilized by inclusion of several solvated  $\text{Li}^+$  ions. In I  $\text{Nb(III)}$  is surrounded in a roughly trigonal bipyramidal fashion by 3 Ph and 2 benzyne groups with 5 associated THF-solvated  $\text{Li}^+$  ions and another Ph group.  $\text{Ta(V)}$  complex II has a distorted octahedral coordination of 4 Ph groups and 2 cis-benzynes with 2 associated solvated  $\text{Li}^+$  ions. Longer C-C distances involving the benzyne ligands suggest that the transition metal centers are fairly electron-rich.

RX(1) OF 2



L6 ANSWER 24 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 108:131538 CASREACT

TITLE: Tandem arylation-reduction of acyl heterocycles. Convenient synthesis of benzyl heterocycles

AUTHOR(S): Hall, Stan S.; Farahat, Sami E.

CORPORATE SOURCE: Dep. Chem., Rutgers, State Univ., Newark, NJ, 07102, USA

SOURCE: Journal of Heterocyclic Chemistry (1987), 24(4), 1205-13

CODEN: JHTCAD; ISSN: 0022-152X

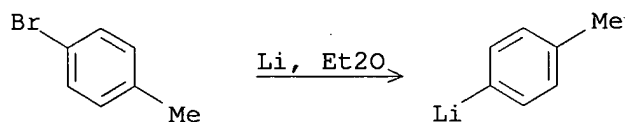
DOCUMENT TYPE: Journal

LANGUAGE: English

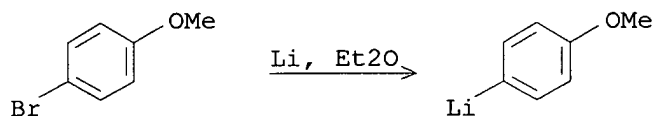
AB Tandem arylation-reduction of a series of acyl heterocycles using  $4\text{-RC}_6\text{H}_4\text{Li}$  ( $\text{R} = \text{H}, \text{Me}, \text{MeO}$ ), followed by  $\text{Li}/\text{NH}_3/\text{NH}_4\text{Cl}$  reduction afforded the corresponding benzyl heterocycles in 38-99% yields. The acyl heterocycles surveyed in this study contained furan, 2,3-dihydro-4H-1-benzopyran, 4H-1-benzopyran, thiophene, 4,5,6,7-tetrahydrobenzo[b]thiophene, 2,3-dihydro-4H-1-benzothiopyran, and pyridine nuclei. All acyl heterocycles yielded the corresponding benzyl heterocycles except

2,3-dihydro-4H-1-benzothiopyran-4-one, which selectively cleaved during reduction to give the corresponding 2-(1-arylpropyl)benzenethiols.

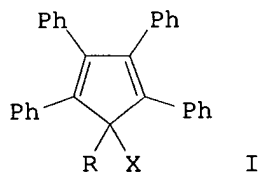
RX(40) OF 81



RX(41) OF 81

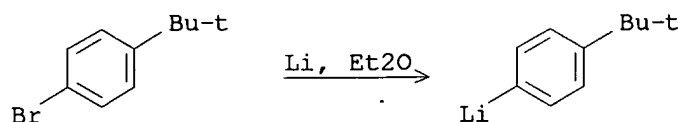


L6 ANSWER 25 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 108:94687 CASREACT  
 TITLE: Tetraphenylcyclopentadiene and (4-tert-butylphenyl)tetraphenylcyclopentadiene: synthesis and characterization of their alkali-metal salts and metallocenes of germanium, tin, and lead  
 AUTHOR(S): Schumann, Herbert; Janiak, Christoph; Zuckerman, Jerold J.  
 CORPORATE SOURCE: Inst. Anorg. Anal. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.  
 SOURCE: Chemische Berichte (1988), 121(2), 207-18  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DOCUMENT TYPE: Journal  
 LANGUAGE: German  
 GI



AB Title compds. I (R = H, Ph, 4-Me<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>; X = H, Li, Na, K, Br, OH) and the Ge, Sn, and Pb metallocenes of I (R = H, 4-Me<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>; X = H) were prepared IR, Raman, <sup>1</sup>H and <sup>13</sup>C NMR and mass spectral data and x-ray powder diagrams were reported. Comparative <sup>13</sup>C NMR studies showed delocalization of the neg. charge from the cyclopentadiene ring into the nonparallel Ph ligands.

RX(22) OF 185



ACCESSION NUMBER: 108:75448 CASREACT

TITLE: Structure of 2-lithiophenyl tert-butyl thioether in solution and in the solid state. Detection of agostic lithium-hydrogen interactions by NMR spectroscopy

AUTHOR(S): Bauer, Walter; Klusener, P. A. A.; Harder, Sjoerd; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, Lambert; Schleyer, Paul v. R.

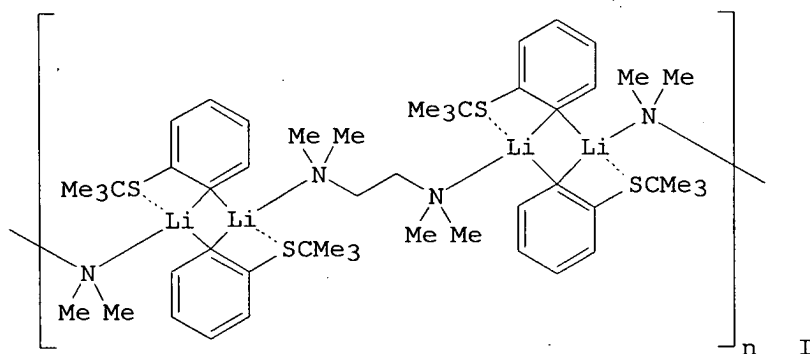
CORPORATE SOURCE: Org. Chem. Lab., Rijksuniv. Utrecht, Utrecht, 3584 CH, Neth.

SOURCE: Organometallics (1988), 7(2), 552-5  
CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal

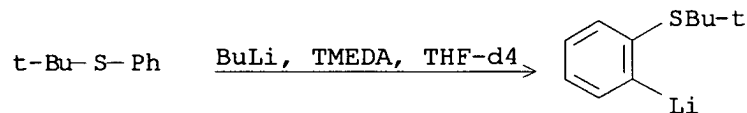
LANGUAGE: English

GI



AB Tert-Bu phenyl thioether, in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA), is deprotonated with BuLi in hexane to give the ortho lithiation product I. X-ray anal. shows I to be an endless polymer with dimeric centrosym. subunits linked by TMEDA acting as a bridging ligand. The lithiated C atom tends toward planar tetracoordination. However, a different structure is present in solution. Structural assignments for I in THF solution are made by one- and two-dimensional NMR spectroscopy. Complete dissociation into monomers is indicated by <sup>13</sup>C NMR (signal multiplicities and <sup>13</sup>C, <sup>6</sup>Li coupling consts.). Close Li-H contacts (detected by <sup>6</sup>Li-<sup>1</sup>H 2D heteronuclear Overhauser spectroscopy, HOESY) are observed for the aromatic H atom vicinal to the Li substituent and for the Me<sub>3</sub>C group. However, TMEDA apparently is not bound to Li in THF solution

RX(2) OF 2



ACCESSION NUMBER: 108:21630 CASREACT

TITLE: Regioselective generation and trapping of mono- and dianions of 3-(arylsulfonyl)furans. Bidentate carbanion stabilization via sulfones

AUTHOR(S): Hartman, George D.; Halczenko, Wasyl

CORPORATE SOURCE: Merck Sharp and Dohme Res. Lab., West Point, PA,

SOURCE:

19486, USA

Tetrahedron Letters (1987), 28(28), 3241-4

CODEN: TELEAY; ISSN: 0040-4039

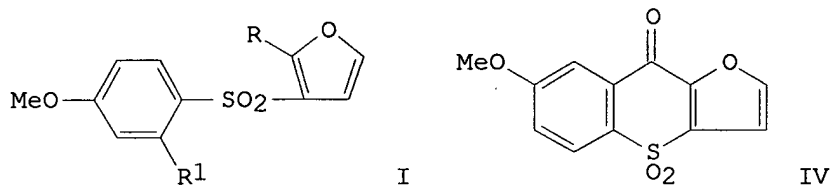
DOCUMENT TYPE:

Journal

LANGUAGE:

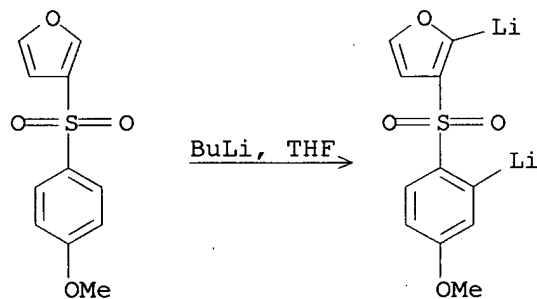
English

GI

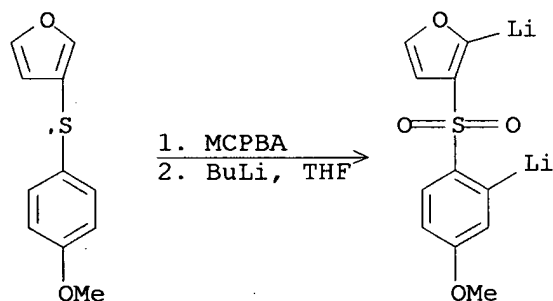


AB Lithiation of methoxyphenylsulfonylfuran I ( $R = R_1 = H$ ) with 1 equivalent BuLi gave lithio derivative I ( $R = Li, R_1 = H$ ), which was trapped with D<sub>2</sub>O or Me<sub>2</sub>N<sup>+</sup>:CH<sub>2</sub> I<sup>-</sup> (II) to give adducts I ( $R = D, CH_2NMe_2, R_1 = H$ ). Lithiation of I ( $R = R_1 = H$ ) with 2 equivalent BuLi regiospecifically gave dilithio derivative I ( $R = R_1 = Li$ ) (III). III was trapped with excess D<sub>2</sub>O or II to give disubstituted adducts I ( $R = R_1 = D, CH_2NMe_2$ ), with 1 equivalent II to give I ( $R = H, R_1 = CH_2NMe_2$ ), and with (EtO)<sub>2</sub>CO to give tricyclic ketone IV.

RX(5) OF 33

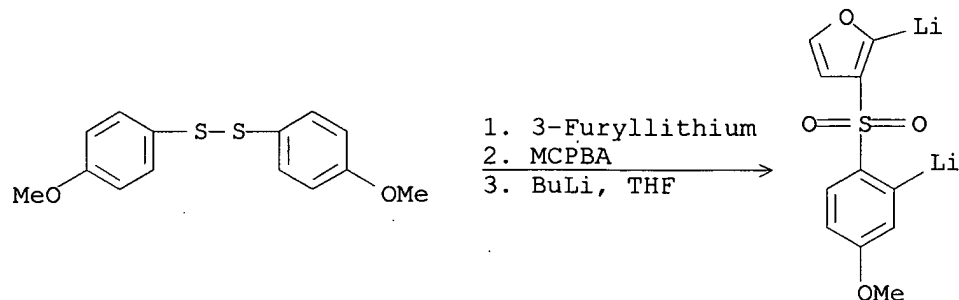


RX(12) OF 33 - 2 STEPS

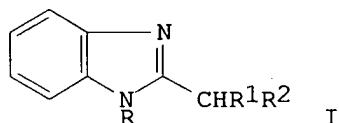




RX(33) OF 33 - 3 STEPS

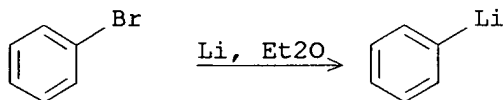


L6 ANSWER 28 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 107:7241 CASREACT  
TITLE: Lithium and sodium derivatives of N-substituted  
2-alkylbenzimidazoles  
AUTHOR(S): Tertov, B. A.; Bogachev, Yu. G.; Koshchienko, Yu. V.;  
Suvorova, G. M.; Tsupak, E. B.; Chub, N. K.; Breus, S.  
F.  
CORPORATE SOURCE: Rostov. Gos. Univ., Rostov, USSR  
SOURCE: Khimiya Geterotsiklicheskikh Soedinenii (1986), (8),  
1073-7  
CODEN: KGSSAQ; ISSN: 0453-8234  
DOCUMENT TYPE: Journal  
LANGUAGE: Russian  
GI



AB The title compds. (I; R = Me, Ph; R1 = H, Me, Et, R2 = Li, Na)  
were prepared in 90-6% yields by metalation of I (R1 = H) with R3Li or R3Na  
(R3 = Bu, Ph, naphthyl). The preparation of other derivs. by treating I (R2 =  
Li, Na) with Ph2CO, PrONO2, aldehydes, and iodides was also  
discussed. Thus, treating I (R = Me, R1 = H, R2 = Na) with MeI gave the  
corresponding I (R2 = Me).

RX(38) OF 82

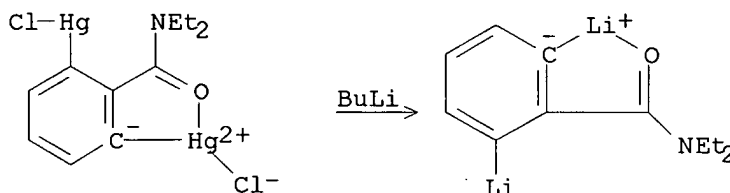


L6 ANSWER 29 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 106:119913 CASREACT  
TITLE: Reverse transmetalation: a strategy for obtaining  
certain otherwise difficultly accessible

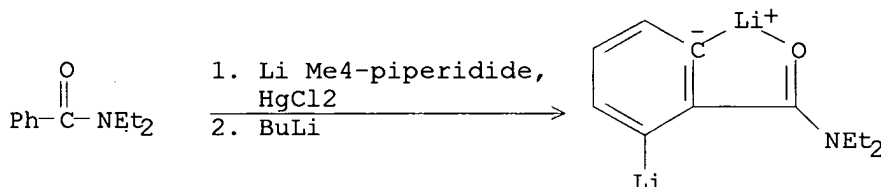
organometallics  
 AUTHOR(S): Eaton, Philip E.; Cunkle, Glen T.; Marchioro, Gaetano; Martin, Ronald M.  
 CORPORATE SOURCE: Dep. Chem., Univ. Chicago, Chicago, IL, 60637, USA  
 SOURCE: Journal of the American Chemical Society (1987), 109(3), 948-9  
 CODEN: JACSAT; ISSN: 0002-7863  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English

AB Li and Grignard derivs. of amide activated cubanes are made in high yield and free of interfering reactants by treatment of the corresponding cubylmercury with CH<sub>3</sub>Li or CH<sub>3</sub>MgBr. As the cubylmercury is obtained by transmetalation trapping of a small equilibrium concentration of the cubyllithium, the process is called reverse transmetalation. Similar organometallics are available using these processes on an amide activated cyclopropane. Double reverse transmetalation is used for the preparation of dilithio and di-Grignard derivs. of a cubane diamide.

RX(1) OF 16



RX(15) OF 16 - 2 STEPS



L6 ANSWER 30 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 106:33276 CASREACT

TITLE: Binding of platinum(II) via a  $\sigma$ -Pt-C bond to a novel type of macrocyclic monoanionic carbodiaza ligand: x-ray crystal structure of

trans[2,6-(2,13-dimethyl-2,13-diazatetradecanediyl)phenyl-N,N']platinum(II) iodide  
 AUTHOR(S): Terheijden, Jos; Van Koten, Gerard; Van Beek, Johannus A. M.; Vriesema, Bindert K.; Kellogg, Richard M.; Zoutberg, Martin C.; Stam, Casper H.

CORPORATE SOURCE: Anorg. Chem. Lab., Univ. Amsterdam, Amsterdam, 1018 WV, Neth.

SOURCE: Organometallics (1987), 6(1), 89-93  
 CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal

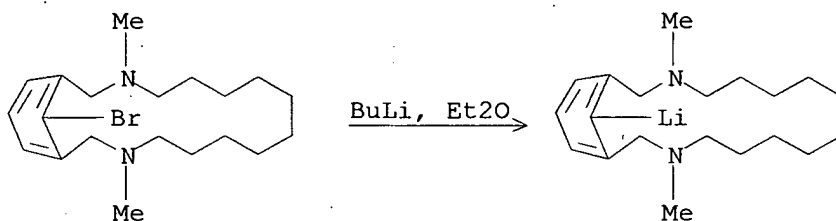
LANGUAGE: English

GI For diagram(s), see printed CA Issue.

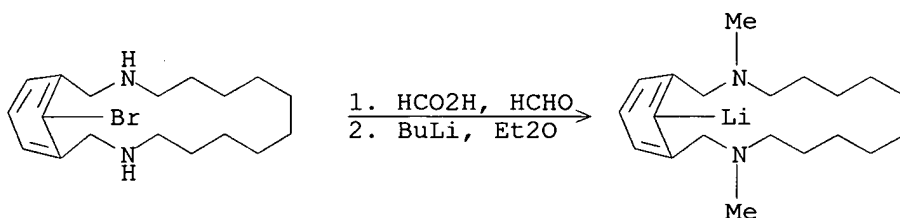
AB The macrocyclic, monoanionic carbodiaza ligand 3,14-diaza-20-bromo-3,14-dimethylbicyclo[14.3.1]eicosa-1(20),16,18-triene (I) was prepared in 55% yield from 2,6-(BrCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Br and p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NH(CH<sub>2</sub>)<sub>10</sub>NHSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-p in the presence of Cs<sub>2</sub>CO<sub>3</sub>. Detosylation with HBr and methylation with HCHO-HCO<sub>2</sub>H afforded I. The organoplatinum complex II is the 1st example of an

organometallic cage compound Its preparation involved reaction of [PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] with the Li derivative of I, followed by halide exchange with NaI in Me<sub>2</sub>CO. II contains a divalent Pt center with the N donor atoms positioned trans owing to the geometric constraints of the terdentate coordination. Single-crystal x-ray diffraction established the structure of II as having a long hydrocarbon chain bending away from the coordination plane.

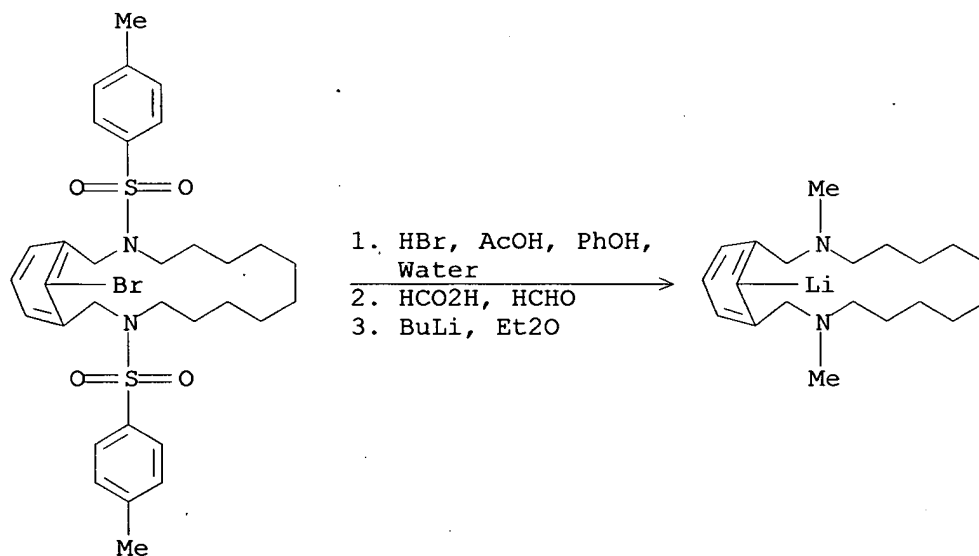
RX(4) OF 15



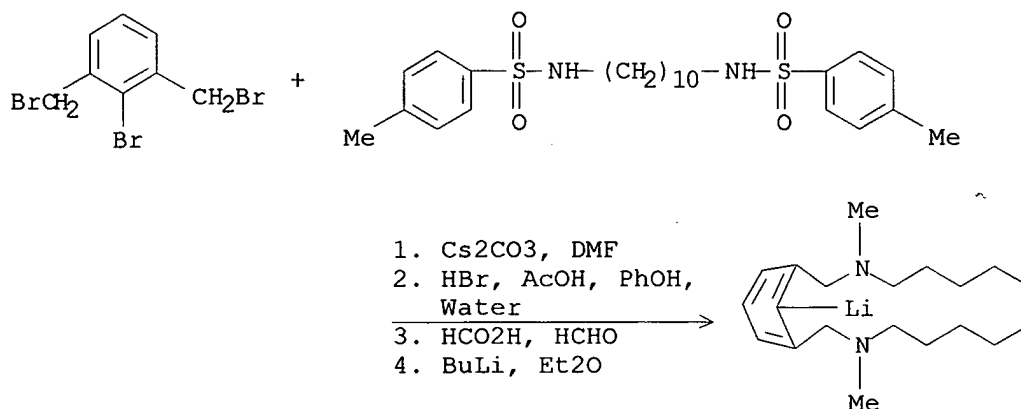
RX(8) OF 15 - 2 STEPS



RX(11) OF 15 - 3 STEPS



RX(12) OF 15 - 4 STEPS



L6 ANSWER 31 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 106:32467 CASREACT

TITLE: Steric consequence of the diastereoselective addition of chiral lithium 2-(1-dimethylaminoethyl)phenyl cuprates to some enones

AUTHOR(S): Andersson, Staffan; Jagner, Susan; Nilsson, Martin; Urso, Fabio

CORPORATE SOURCE: Dep. Inorg. Chem., Chalmers Univ. Technol., Goeteborg, S-412 96, Swed.

SOURCE: Journal of Organometallic Chemistry (1986), 301(2), 257-67

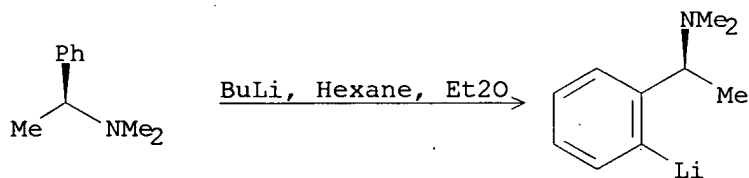
CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Conjugate addition of the chiral Li [(S)-2-(1-dimethylaminoethyl)phenyl] (2-thienyl) cuprate to (E)-4-phenyl-3-buten-2-one, 2-cyclohexenone or 2-cyclopentenone gave with high diastereoselectivity (S,S)-4-[2-(1-dimethylaminoethyl)phenyl]-4-phenyl-2-butenone, (S,S)-3-[2-(1-dimethylaminoethyl)phenyl]-2-cyclohexanone, and (S,S)-1-[3-oxocyclopentyl]phenyl ethyltrimethylammonium iodide. The (S,S)-configuration observed in the adducts indicated that the conjugate addition gave the least crowded Li enolate as the major product.

RX(1) OF 16



L6 ANSWER 32 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 105:208987 CASREACT

TITLE: New methods for the synthesis of proximally functionalized arylboranes and silanes

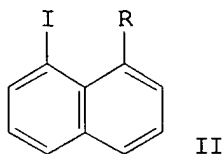
AUTHOR(S): Katz, H. E.

CORPORATE SOURCE: AT and T Bell Lab., Murray Hill, NJ, 07974, USA

SOURCE: Organometallics (1986), 5(11), 2308-11

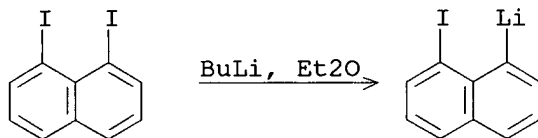
CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE: Journal  
LANGUAGE: English  
GI



AB The synthesis of ten novel disubstituted aromatic compds. is reported. New methods that were developed for the syntheses include (1) single I-Li exchange of 1,8-diiodonaphthalene, (2) use of  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$  (I) to form C-Si bonds in sterically hindered situations, and (3) protection of an organoborane as an ethoxy ate complex during halogen-metal exchange and substitution on the organic residue. In addition, the dimethylborylation of aryllithium reagents with  $\text{Me}_2\text{BOEt}$  was generalized to include labile nucleophiles. The methods are geared to the synthesis of perisubstituted naphthalenes as anion receptors but should be of more general utility as well. Finally, some special properties of the newly synthesized compds. are discussed. E.g., the reaction of iodonaphthalene derivative II ( $\text{R} = \text{Li}$ ) with I,  $\text{B}(\text{OEt})_3$ , and  $\text{EtOBMe}_2$  gave 65-83% I [ $\text{R} = \text{SiMe}_3$ ,  $\text{B}(\text{OEt})_2$ ,  $\text{BMe}_2$ ], resp.

RX(1) OF 28



L6 ANSWER 33 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 105:24745 CASREACT

TITLE: Quaternized cyclic and high polymeric phosphazenes and their interactions with tetracyanoquinodimethane

AUTHOR(S): Allcock, Harry R.; Levin, Michael L.; Austin, Paul E.

CORPORATE SOURCE: Dep. Chem., Pennsylvania State Univ., University Park, PA, 16802, USA

SOURCE: Inorganic Chemistry (1986), 25(14), 2281-8

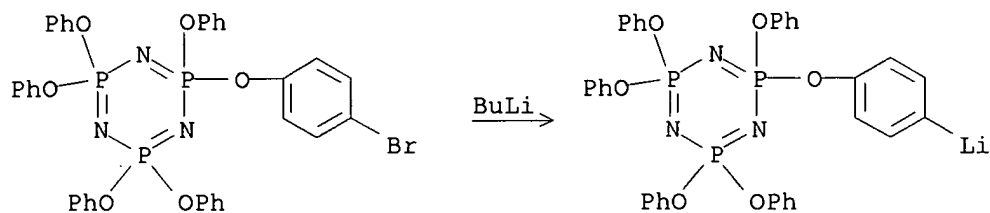
CODEN: INOCAJ; ISSN: 0020-1669

DOCUMENT TYPE: Journal

LANGUAGE: English

AB Small-mol. cyclotri- or cyclotetraphosphazenes and their linear high polymeric analogs bearing amino, phosphino, or organohalo side groups were quaternized by treatment with  $\text{MeI}$  or  $\text{Ph}_3\text{P}$ . Quaternization occurred at the side-group sites except with the piperidino derivs., where the reactive sites were the skeletal nitrogen atoms. The quaternized species reacted with Li 7,7,8,8-tetracyanoquinodimethane [1283-90-5] to generate TCNQ "simple salts", and these (or their onium precursors) reacted with neutral TCNQ to generate the "complex salts". The elec. conductivities of the cyclic trimeric phosphazene complex salts ( $10^{-3}$ - $10^{-2} \Omega^{-1} \text{cm}^{-1}$ ) were higher than those of their high polymeric counterparts.

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L6 ANSWER 34 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 104:68510 CASREACT

TITLE: Dianion metalation reactions of N,N-dimethylvanillylamine and N,N-dimethylisovanillylamine

AUTHOR(S): Hlasta, Dennis J.; Bell, Malcolm R.

CORPORATE SOURCE: Sterling-Winthrop Res. Inst., Rensselaer, NY, 12144, USA

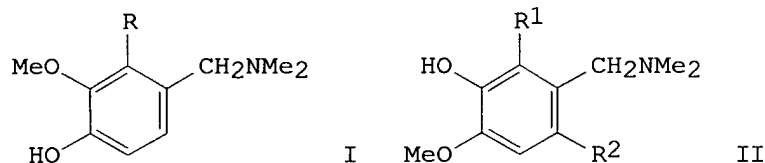
SOURCE: Tetrahedron Letters (1985), 26(18), 2151-4

CODEN: TELEAY; ISSN: 0040-4039

DOCUMENT TYPE: Journal

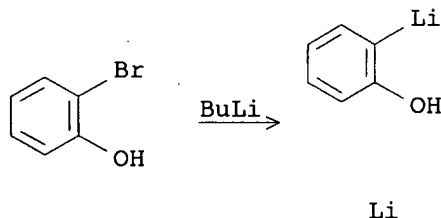
LANGUAGE: English

GI



AB The utility of dianion chemical in the synthesis of polyfunctional aroms. is demonstrated by the direct lithiation of the vanillylamine I (R = H) and by the Li-Br exchange reaction of isovanillylamines II (R<sub>1</sub> = H, R<sub>2</sub> = Br; R<sub>1</sub> = Br, R<sub>2</sub> = H). Condensation of the lithiated dianions with Ph<sub>2</sub>CO and 4-PhCH<sub>2</sub>OC<sub>6</sub>H<sub>4</sub>CHO yielded I [R = CPh<sub>2</sub>OH, CH(OH)C<sub>6</sub>H<sub>4</sub>OCH<sub>2</sub>Ph-4] and II (R<sub>1</sub> = H, R<sub>2</sub> = CPh<sub>2</sub>OH; R<sub>1</sub> = CPh<sub>2</sub>OH, R<sub>2</sub> = H). Lithiation and subsequent reaction with D<sub>2</sub>O yielded no detectable dianion formation for II (R<sub>1</sub>, R<sub>2</sub> = H), 2-HOC<sub>6</sub>H<sub>4</sub>OMe, and 4-HOC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>.

RX(4) OF 6



L6 ANSWER 35 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 104:34182 CASREACT

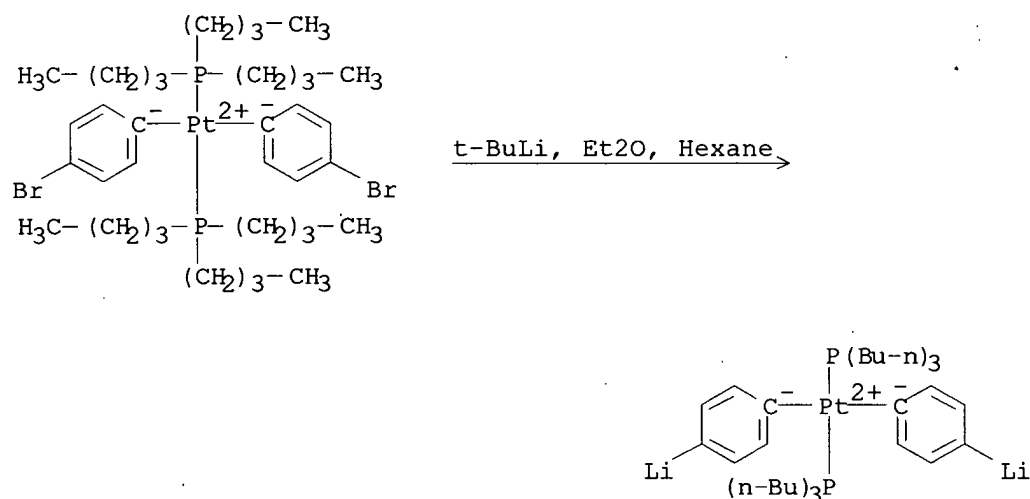
TITLE: Syntheses of cis- and trans-bis(substituted

phenyl)bis(tributylphosphine)platinum(II) compounds with substituents of  $\pi$ -acceptor character in the platinum-bound phenyl rings

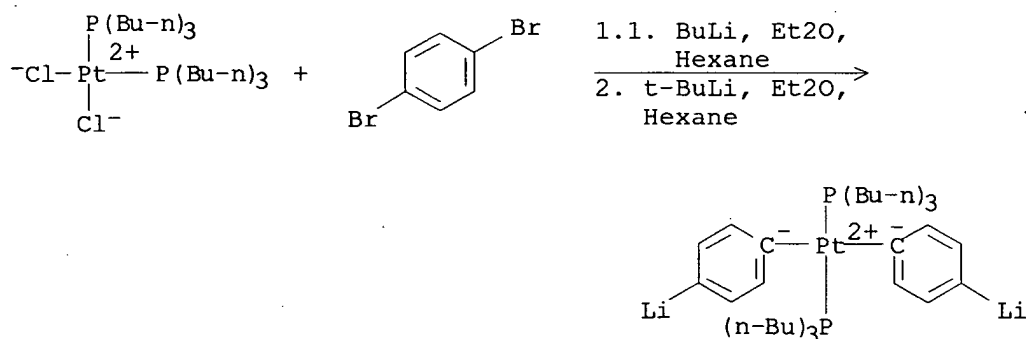
AUTHOR(S): Mueller, Wolf Dieter; Brune, Hans Albert  
 CORPORATE SOURCE: Abt. Theor. Chem., Univ. Ulm, Ulm/Donau, D-7900, Fed. Rep. Ger.  
 SOURCE: Chemische Berichte (1985), 118(11), 4347-55  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DOCUMENT TYPE: Journal  
 LANGUAGE: German

AB cis-[Pt(PBu<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>R-p)<sub>2</sub>] (cis-I; R = D, SiMe<sub>3</sub>, CO<sub>2</sub>H, CO<sub>2</sub>Me, cyano, CPh) and trans-I (R = iodo) were prepared by treating cis-I (R = Li) with suitable reagents. cis-I were converted to trans-I by catalysis with Bu<sub>4</sub>N<sup>+</sup> I<sup>-</sup>.

RX(15) OF 48



RX(23) OF 48 - 2 STEPS



L6 ANSWER 36 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 102:166432 CASREACT

TITLE: Possibilities and limits of the anionically induced sulfonamide-amino sulfone rearrangement

AUTHOR(S): Hellwinkel, Dieter; Lenz, Ruediger

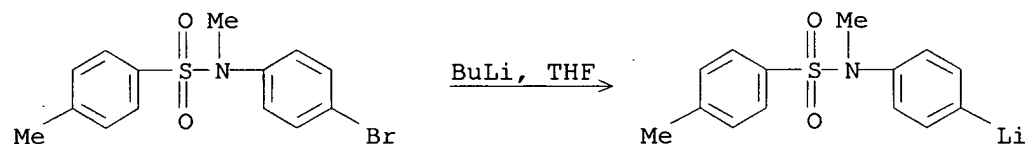
CORPORATE SOURCE: Org.-Chem. Inst., Univ. Heidelberg, Heidelberg, D-6900/1, Fed. Rep. Ger.

SOURCE: Chemische Berichte (1985), 118(1), 66-85  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DOCUMENT TYPE: Journal  
 LANGUAGE: German  
 GI

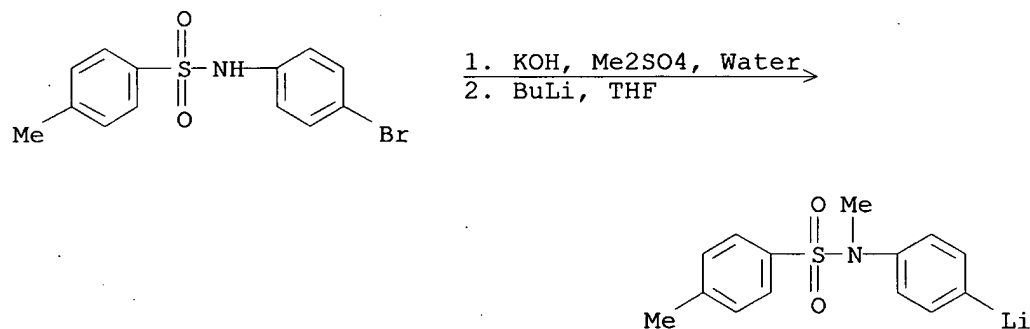
\* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT \*

AB When applying the title reaction to naphthyltoluenesulfonamides I (N at 1, 2), the [1,3] shift of the arylsulfonyl group proceeds to the 3- and 2-position, to give II and III (R = H), resp., which is in full compliance with optimal conjugative and steric conditions for the relevant intermediates II and III (R = Li). Attempts to initiate comparable [1,5] rearrangements via the o-lithiated biphenyl derivative IV and p-lithiated 4-LiC<sub>6</sub>H<sub>4</sub>NMeSO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4 gave, after extended transmetalation cascades, conventional [1,3] rearrangement products V and 2-MeNHC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Me-4, resp. While attempting to cause an anionically-induced [1,4] sulfonyl shift in 2-MeC<sub>6</sub>H<sub>4</sub>NMeSO<sub>2</sub>Ph (VI) into the benzyl position, 2 fragments of VI combined to give the novel heteropolycycle VII. Contrary to the literature, sulfonamides VIII (R<sub>1</sub> = H, Me) also rearranged photolytically to o-amino sulfones IX.

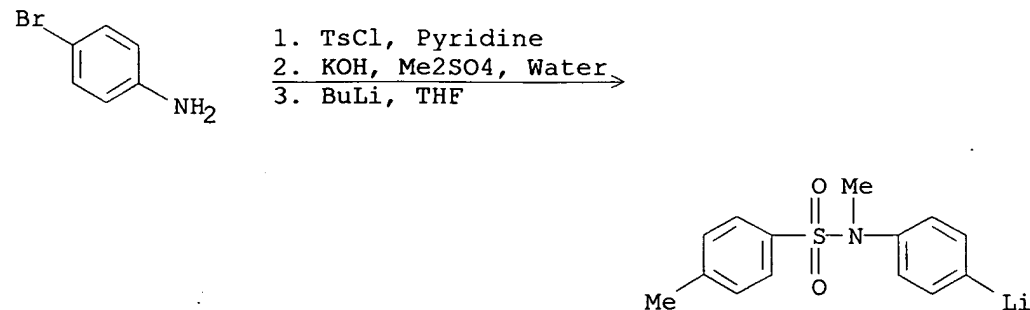
RX(19) OF 86



RX(51) OF 86 - 2 STEPS

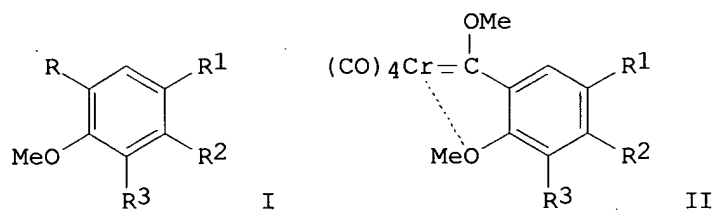


RX(74) OF 86 - 3 STEPS



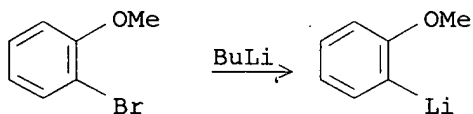


L6 ANSWER 37 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 102:113657 CASREACT  
 TITLE: Carbene ligands as anthracyclinone synthons. I.  
 Methoxyarylcabene as chelating ligands  
 AUTHOR(S): Doetz, Karl Heinz; Sturm, Werner; Popall, Michael;  
 Riede, Juergen  
 CORPORATE SOURCE: Anorg. Chem. Inst., Tech. Univ. Muenchen, Garching,  
 D-8046, Fed. Rep. Ger.  
 SOURCE: Journal of Organometallic Chemistry (1984), 277(2),  
 267-75  
 CODEN: JORCAI; ISSN: 0022-328X  
 DOCUMENT TYPE: Journal  
 LANGUAGE: German  
 GI

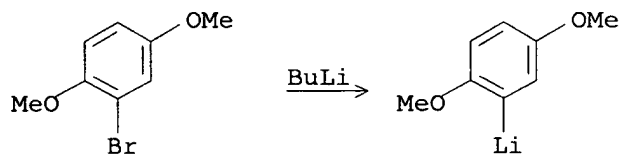


AB Pentacarbonyl[methoxy(1-methoxy-2-aryl)carbene]chromium complexes I [ $R = C(OMe):Cr(CO)_5$ ;  $R_1 = H$ ,  $OMe$ ,  $R_2 = R_3 = H$ ,  $R_2R_3 = CH:CHCH:CH$ ;  $R_1 = R_3 = H$ ,  $R_2 = OMe$ ] are obtained via successive addition of I ( $R = Li$ ) and  $Me_3O+BF_4^-$  to  $Cr(CO)_6$ . I [ $R = C(OMe):Cr(CO)_5$ ] undergo intramol. CO-substitution to give cis-tetracarbonyl[methoxy(1-methoxy-2-aryl)carbene] complexes II. Coplanarity of the "chromabenzofuran" system was established by x-ray anal. of II ( $R_1-R_3 = H$ ). II analogs have been used as synthons for anthracyclinones.

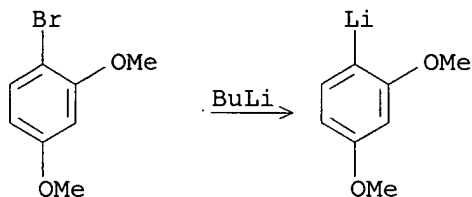
RX(1) OF 4



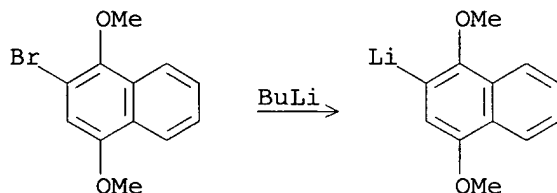
RX(2) OF 4



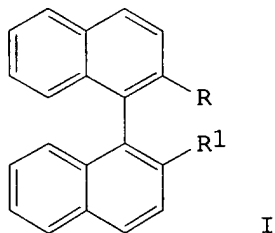
RX(3) OF 4



RX(4) OF 4



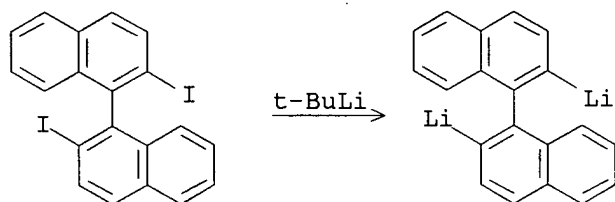
L6 ANSWER 38 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 101:90538 CASREACT  
TITLE: Preparation and lithiation of optically active 2,2'-dihalo-1,1'-binaphthyls. A general strategy for obtaining chiral, bidentate ligands for use in asymmetric synthesis  
AUTHOR(S): Brown, Kenneth J.; Berry, Matthew S.; Waterman, Kenneth C.; Lingenfelter, David; Murdoch, Joseph R.  
CORPORATE SOURCE: Dep. Chem. Biochem., Univ. California, Los Angeles, CA, 90024, USA  
SOURCE: Journal of the American Chemical Society (1984), 106(17), 4717-23  
CODEN: JACSAT; ISSN: 0002-7863  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
GI



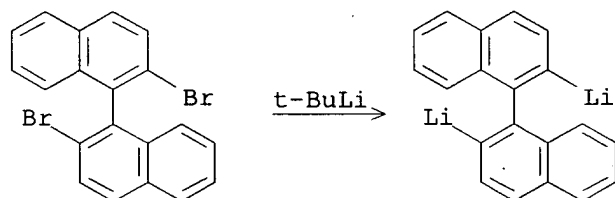
AB Binaphthyls I (R = R<sup>1</sup> = Br, iodo) of up to 98% optical purity were mono- or dilithiated to give I (R = Li, R<sup>1</sup> = Li, Br, iodo), which were configurationally stable from -131 to up to at least -44°. (R)-I (R = R<sup>1</sup> = iodo) with 43.7 ± 1, 48.1 ± 2, and >98% ee (ee = enantiomeric excess) reacted with PhCHO to give 42.7 ± 3, 47.2 ± 3, and >98% ee, resp., (R)-I (R = HOCHPh, R<sup>1</sup> = H). (R)- And (S)-I (R = R<sup>1</sup> = iodo) with 88.5 ± 5 and 57.7 ± 3% ee, resp., gave

(R)- and (S)-I (R = R1 = PPh<sub>2</sub>) with 86.5 ± 1 and 57.2 ± 1% ee upon treatment with ClPPh<sub>2</sub>.

RX(2) OF 4



RX(3) OF 4



L6 ANSWER 39 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 100:6594 CASREACT

TITLE: Regioselective metalation of aromatic compounds. II. Second metalation and 1-lithionaphthalene and 9-lithioanthracene.

AUTHOR(S): Neugebauer, Wolfgang; Clark, Timothy; Schleyer, Paul v. R.

CORPORATE SOURCE: Inst. Org. Chem., Univ. Erlangen-Nurnberg, Erlangen, D-8520, Fed. Rep. Ger.

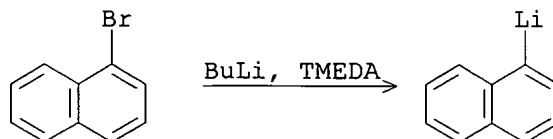
SOURCE: Chemische Berichte (1983), 116(10), 3283-92  
CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal

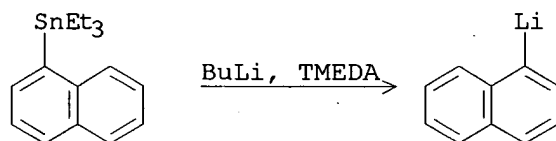
LANGUAGE: German

AB Both 1-lithionaphthalene and 9-lithioanthracene undergo specific metalations whereby a second Li is introduced at the adjacent peri-positions in the presence of BuLi-Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>. Explanations for such directed second metalations, for which other examples are known, are provided by MNDO calcs. The dilithiated products are stabilized by sym. double bridging. The LUMO coeffs. on the activated H in the monolithio precursors are largest and the C-H bond lengths longest. Dimers, more realistic models for the solution species, show these characteristics as well.

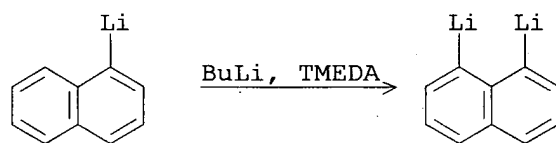
RX(10) OF 51



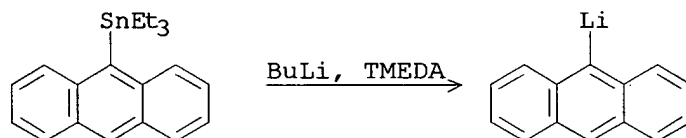
RX(11) OF 51



RX(12) OF 51



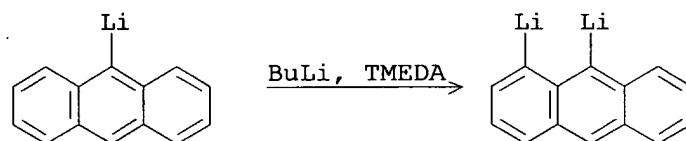
RX(14) OF 51



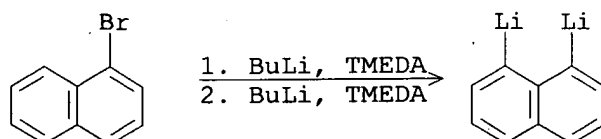
RX(15) OF 51



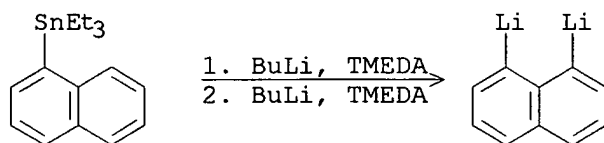
RX(16) OF 51



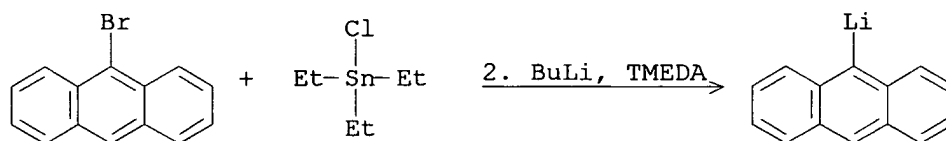
RX(21) OF 51 - 2 STEPS



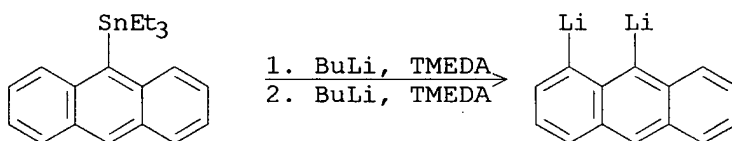
RX(24) OF 51 - 2 STEPS



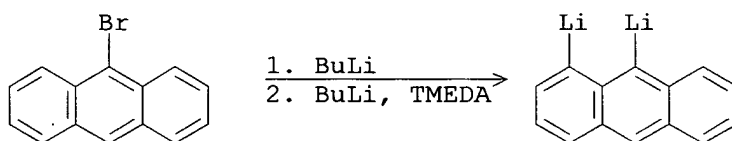
RX(27) OF 51 - 2 STEPS



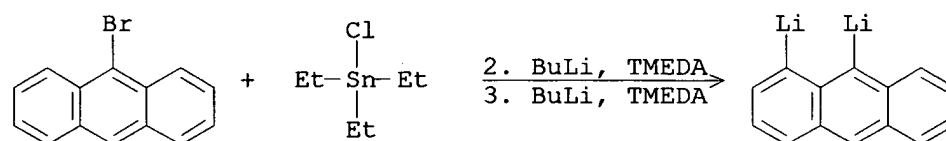
RX(30) OF 51 - 2 STEPS



RX(33) OF 51 - 2 STEPS



RX(45) OF 51 - 3 STEPS



L6 ANSWER 40 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 99:175902 CASREACT

TITLE: Reactions of lithium o-lithiophenolate and lithium o-lithio-N-methylanilide with halides of phosphorus, arsenic and silicon

AUTHOR(S): Heinicke, J.; Tzschach, A.

CORPORATE SOURCE: Sekt. Chem., Martin-Luther-Univ. Halle-Wittenberg, Halle/Saale, DDR-4020, Ger. Dem. Rep.

SOURCE: Journal fuer Praktische Chemie (Leipzig) (1983), 325(2), 232-7

CODEN: JPCEAO; ISSN: 0021-8383

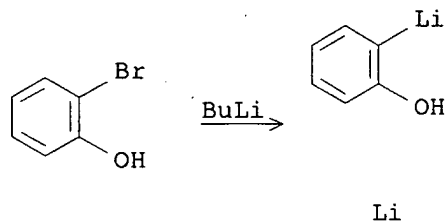
DOCUMENT TYPE: Journal

LANGUAGE: German

AB Approx. 10 arsino- and silylphenol derivs. and arsino- and

phosphinoanilides were prepared by the reaction of the title compds. with chloroarsines, chlorosilanes, and chlorophosphines. Thus, o-LiC<sub>6</sub>H<sub>4</sub>OLi and Me<sub>3</sub>CAsCl<sub>2</sub> gave Me<sub>3</sub>CAs(C<sub>6</sub>H<sub>4</sub>OLi-o)<sub>2</sub>, which, with Me<sub>3</sub>CSiCl, gave 60% Me<sub>3</sub>CAs(C<sub>6</sub>H<sub>4</sub>OSiMe<sub>3</sub>-o)<sub>2</sub>. Similarly, o-LiC<sub>6</sub>H<sub>4</sub>N(Li)Me and ClP(NMe<sub>2</sub>)<sub>2</sub> gave 72% o-(Me<sub>2</sub>N)<sub>2</sub>PC<sub>6</sub>H<sub>4</sub>[NMeP(NMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>.

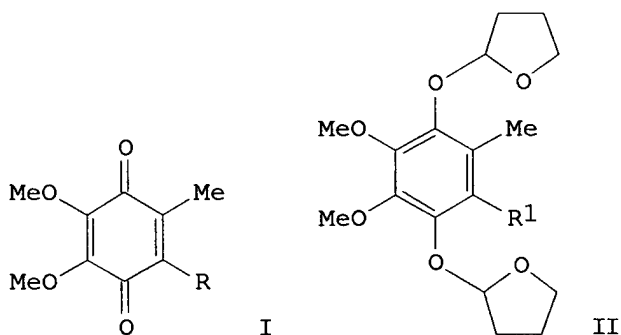
RX(2) OF 11



L6 ANSWER 41 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 99:158685 CASREACT  
 TITLE: Coenzymes Q  
 PATENT ASSIGNEE(S): Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical Research Institute  
 SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.  
 CODEN: JKXXAF  
 DOCUMENT TYPE: Patent  
 LANGUAGE: Japanese  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

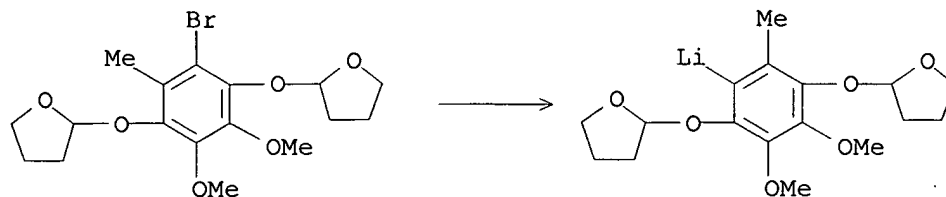
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 58041839	A	19830311	JP 1981-139669	19810907
PRIORITY APPLN. INFO.:			JP 1981-139669	19810907

GI



AB Title compds. (I, R = solanesyl, decaprenyl, geranyl, phytlyl) were prepared by alkylation of II (R<sub>1</sub> = Li) with RBr and subsequent hydrolysis and oxidation. Thus, treatment of 350 mg solanesyl bromide in THF with II (R<sub>1</sub> = Li), obtained from 400 mg II (R<sub>1</sub> = Br), at -60° for 2 h and at -60 to 0° for 15 h gave 740 mg II (R<sub>1</sub> = solanesyl), whose acid hydrolysis followed by Ag<sub>2</sub>O oxidation gave I (R = solanesyl).

RX(2) OF 5



L6 ANSWER 42 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 99:104903 CASREACT

TITLE: Regiospecific synthesis of aromatic compounds via organometallic intermediates. I. para-Substituted benzenes.

AUTHOR(S): Chen, Loomis S.; Chen, Grace J.; Tamborski, Christ

CORPORATE SOURCE: Mater. Lab., Air Force Wright Aeronaut. Lab., Wright-Patterson Air Force Base, OH, 45433, USA

SOURCE: Journal of Organometallic Chemistry (1983), 251(2), 139-48

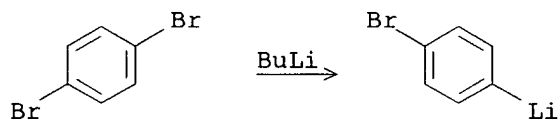
CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

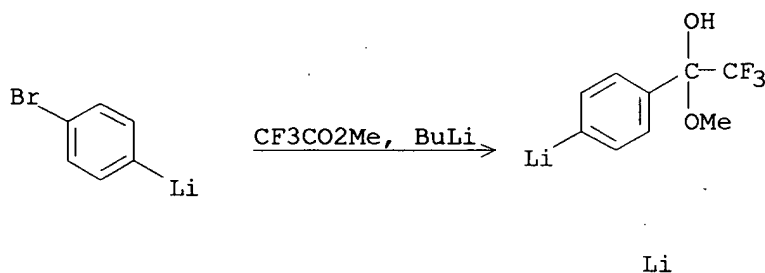
LANGUAGE: English

AB 4-RC<sub>6</sub>H<sub>4</sub>COCF<sub>3</sub> (R = H, Me, CO<sub>2</sub>H, COMe, COCF<sub>3</sub>, CHO, SH) were prepared by sequential metal-halogen exchange between 1,4-Br<sub>2</sub>C<sub>6</sub>H<sub>4</sub> and BuLi and electrophiles. Low reaction temperature is critical to stabilization of the various intermediates. The CF<sub>3</sub> group has a pronounced effect on stabilizing the Li hemiketal intermediates.

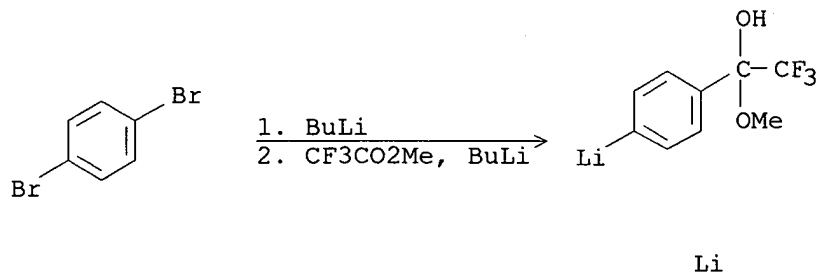
RX(2) OF 29



RX(11) OF 29



RX(13) OF 29 - 2 STEPS



L6 ANSWER 43 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 97:38583 CASREACT

TITLE: Reactions of methylcopper and chiral organocuprates with 1-nitro-2-phenylethene and of lithium dimethylcuprate with methyl 3-(nitrophenyl)propenoates

AUTHOR(S): Hansson, A. T.; Nilsson, M.

CORPORATE SOURCE: Dep. Org. Chem., Chalmers Univ. Technol., Goeteborg, S-412 96, Swed.

SOURCE: Tetrahedron (1982), 38(3), 389-91

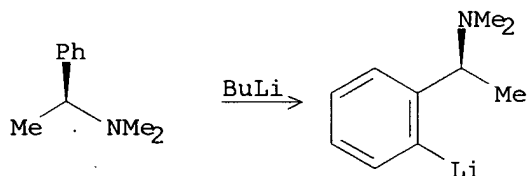
CODEN: TETRAB; ISSN: 0040-4020

DOCUMENT TYPE: Journal

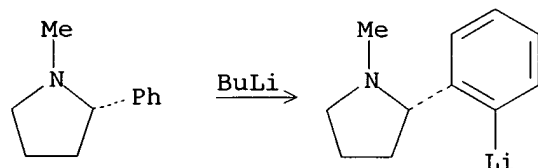
LANGUAGE: English

AB Organometallic compds., e.g. MeCu, LiCuMe<sub>2</sub>, S-(2-Me<sub>2</sub>NCHMeC<sub>6</sub>H<sub>4</sub>)CuMeLi (I), and Li menthoxyethylcuprate reacted with E-PhCH:CHNO<sub>2</sub> (II) to give PhCHMeCH<sub>2</sub>NO<sub>2</sub> (III) in moderate yields. E.g., treatment of II with I in dry Et<sub>2</sub>O at -40° gave 22% III with 2% enantiomeric excess. Treatment of p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH:CHCO<sub>2</sub>Me (p-IV) with LiCuMe<sub>2</sub> gave the corresponding azoxy compound, whereas m-IV with LiCuMe<sub>2</sub> gave some conjugate addition

RX(18) OF 97



RX(21) OF 97



L6 ANSWER 44 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 97:6353 CASREACT

TITLE: Regioselective dimetalation of aromatic compounds. Easy access to 2,2'-disubstituted biphenyl derivatives

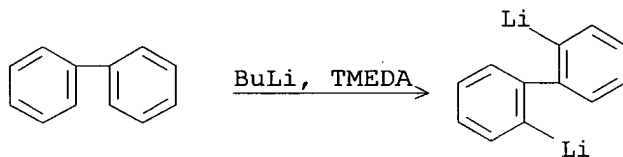
AUTHOR(S): Neugebauer, Wolfgang; Kos, Alexander J.; Schleyer, Paul von Rague



CORPORATE SOURCE: Inst. Org. Chem., Friedrich-Alexander-Univ.  
Erlangen-Nuernberg, Erlangen, D-8520, Fed. Rep. Ger.  
SOURCE: Journal of Organometallic Chemistry (1982), 228(2),  
107-18  
CODEN: JORCAI; ISSN: 0022-328X  
DOCUMENT TYPE: Journal  
LANGUAGE: German

AB Lithiation of biphenyl with 2.4 mol BuLi in the hexane containing Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub> gave 2,2'-dilithiobiphenyl(I) in modest, but preparatively useful yields. I was converted into a variety of products. The activation of the 2'-position of 2-lithiobiphenyl was shown directly by a sep. experiment MNDO calcns. indicate stabilization in I by double bridging and in 2-lithiobiphenyl by intramol.  $\pi$ -interaction of the Li atom with the o-Ph group. Similar interactions in substitution transition states rationalize the specificity of the reactions observed

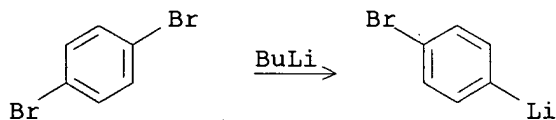
RX(2) OF 10



L6 ANSWER 45 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 96:34746 CASREACT  
TITLE: Fluoro ketones. V. Reactions of alkyl and  
aryllithium compounds with perfluoroalkyl ether esters  
AUTHOR(S): Chen, Loomis S.; Tamborski, Christ  
CORPORATE SOURCE: Mater. Lab., Air Force Wright Aeronaut. Lab., Wright  
Patterson AFB, OH, 45433, USA  
SOURCE: Journal of Fluorine Chemistry (1981), 19(1), 43-53  
CODEN: JFLCAR; ISSN: 0022-1139  
DOCUMENT TYPE: Journal  
LANGUAGE: English

AB BuLi and aryllithium compds. reacted with a perfluoroalkyl ether ester at -78° to produce perfluoroalkyl ether ketones. Steric hindrance adjacent to the carbonyl group has an important effect on rates of reactions. Low reaction temperature is an important factor when secondary esters are used. At >-30° the decreased yields of ketone was due to the instability of the intermediate Li salt of the hemiketal which decomposed to an aryl ester and a perfluorinated olefin.

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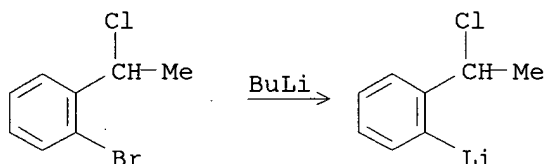
L6 ANSWER 46 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 96:6277 CASREACT  
TITLE: Selective halogen-lithium exchange in some secondary  
and tertiary (bromophenyl)alkyl halides  
AUTHOR(S): Parham, William E.; Bradsher, Charles K.; Reames,  
David C.  
CORPORATE SOURCE: Paul M. Gross Chem. Lab., Duke Univ., Durham, NC,  
27706, USA

SOURCE: Journal of Organic Chemistry (1981), 46(23), 4804-6  
 CODEN: JOCEAH; ISSN: 0022-3263  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English

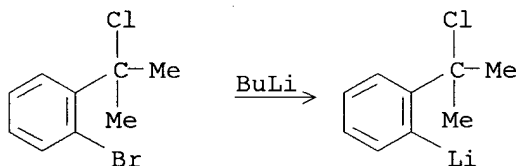
GI For diagram(s), see printed CA Issue.

AB At  $-100^{\circ}$  I (R = H, Me; R1 = Me) undergo efficient selective Br-Li exchange to give the corresponding II which, like, II (R = R1 = H) [from I (R = R1 = H)], react with cyclohexanone to give an anion which cyclizes spontaneously to give III (R = H, Me); III (R = H) is formed in higher yield than III (R = Me). IV (R = Me), derived from V (R = Me) cyclizes more slowly and in poorer yield than does its analog IV (R = H).

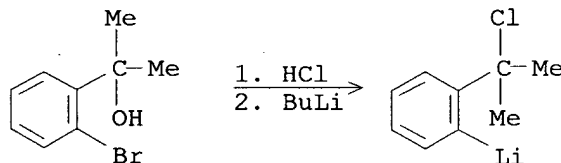
RX(7) OF 26



RX(8) OF 26



RX(15) OF 26 - 2 STEPS



L6 ANSWER 47 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 95:132382 CASREACT

TITLE: Regiospecific functionalization of unsaturated compounds via their dilithio derivatives. Part III. Synthesis of o-halophenylacetylenes via the dianion of phenylacetylene

AUTHOR(S): Hommes, H.; Verkruijsse, H. D.; Brandsma, L.

CORPORATE SOURCE: Dep. Org. Chem., Univ. Utrecht, Utrecht, 3522 AD, Neth.

SOURCE: Tetrahedron Letters (1981), 22(26), 2495-6

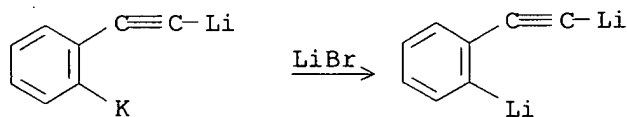
CODEN: TELEAY; ISSN: 0040-4039

DOCUMENT TYPE: Journal

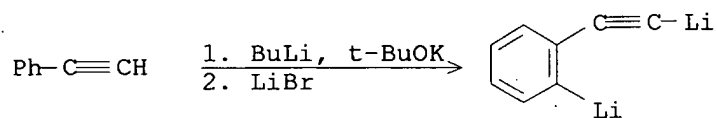
LANGUAGE: English

AB o-RC6H4C.tplbond.CH (R = iodo, Br, Cl) were prepared by reaction of iodine, Br2, and C2Cl6, resp., with o-RC6H4C.tplbond.CR (R = Li, BrMg). E.g., treatment of o-MgBrC6H4C.tplbond.CMgBr with 1 equiv iodine (THF,  $-60^{\circ}$ ) followed by aqueous workup gave 71% o-IC6H4C.tplbond.CH.

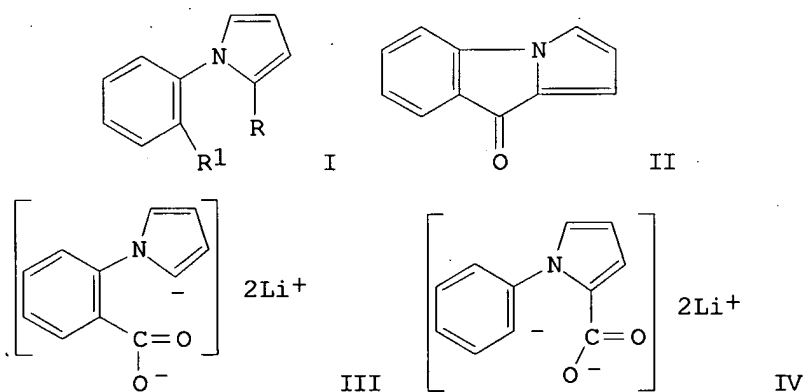
RX(8) OF 19



RX(11) OF 19 - 2 STEPS

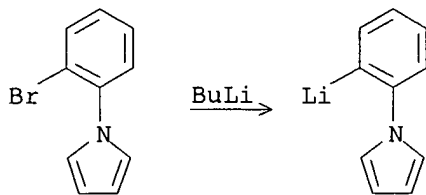


L6 ANSWER 48 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 95:80631 CASREACT  
 TITLE: Lithiation reactions of 1-(2'-bromophenyl)pyrrole and related compounds  
 AUTHOR(S): Cartoon, M. E. K.; Cheeseman, G. W. H.  
 CORPORATE SOURCE: Dep. Chem., Queen Elizabeth Coll., London, W8 7AH, UK  
 SOURCE: Journal of Organometallic Chemistry (1981), 212(1), 1-9  
 CODEN: JORCAI; ISSN: 0022-328X  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI

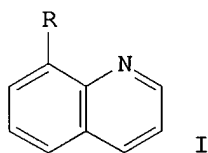


AB Treatment of the phenylpyrroles I ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{CO}_2\text{H}$ ;  $\text{R} = \text{CO}_2\text{H}$ ,  $\text{R}^1 = \text{Br}$ ) with  $\text{LiN}(\text{CHMe}_2)_2$  or  $\text{BuLi}$  gave the pyrroloindolone II, presumably via the dilithio intermediates III or IV, resp. Reaction of the (lithiophenyl)pyrrole I ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{Li}$ ), generated from I ( $\text{R} = \text{H}$ ,  $\text{R}^1 = \text{Br}$ ) and  $\text{BuLi}$  at  $-80^\circ$ , with  $\text{Ph}_2\text{CO}$ ,  $\text{BzH}$ ,  $\text{BzCl}$ ,  $\text{PhCN}$ ,  $\text{EtO}_2\text{CCl}$ , and  $\text{PhO}_2\text{CCl}$  gave I ( $\text{R} = \text{H}$ ;  $\text{R}^1 = \text{CPh}_2\text{OH}$ ,  $\text{CHPhOH}$ ,  $\text{COPh}$ ,  $\text{CPh:NH}$ ,  $\text{CO}_2\text{Et}$ ,  $\text{CO}_2\text{Ph}$ ) in fair to good yields.

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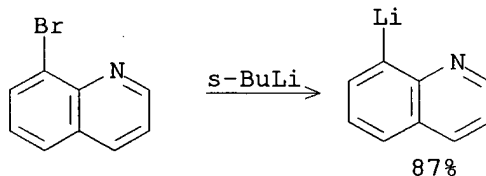


L6 ANSWER 49 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 92:215240 CASREACT  
TITLE: Facile synthesis of 8-substituted quinolines  
AUTHOR(S): Suggs, J. William; Pearson, G. D. N.  
CORPORATE SOURCE: Bell Lab., Murray Hill, NJ, 07974, USA  
SOURCE: Journal of Organic Chemistry (1980), 45(8), 1514-15  
CODEN: JOCEAH; ISSN: 0022-3263  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
GI

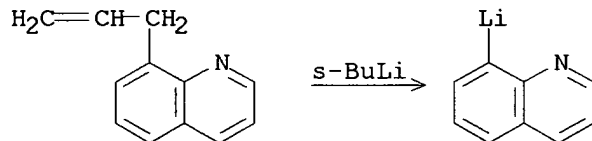


AB The title compds. I (R = CDO, CHO, CHMe(OH), CH<sub>2</sub>CH:CH<sub>2</sub>, PPh<sub>2</sub>, Me, SnMe<sub>3</sub>, CH<sub>2</sub>CH<sub>2</sub>OH) were prepared in 32-87% yields by lithiating I (R = Br) with MeEtCHLi to give I (R = Li) followed by treatment with the appropriate electrophile, e.g., MeI.

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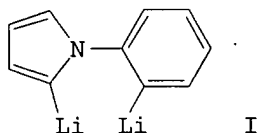


RX(3) OF 25



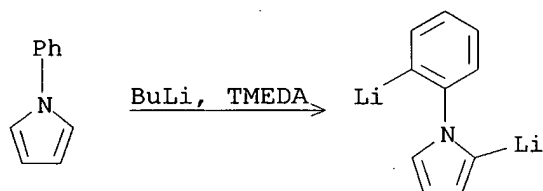
L6 ANSWER 50 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 90:168659 CASREACT  
TITLE: Preparation and reactivity of 2,2'-dilithio-1-phenylpyrrole  
AUTHOR(S): Cheeseman, G. W. H.; Greenberg, S. G.  
CORPORATE SOURCE: Dep. Chem., Queen Elizabeth Coll., London, UK

SOURCE: Journal of Organometallic Chemistry (1979), 166(2), 139-52  
 CODEN: JORCAI; ISSN: 0022-328X  
 DOCUMENT TYPE: Journal  
 LANGUAGE: English  
 GI

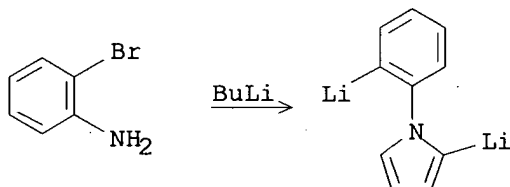


AB The title compound (I) was prepared by lithiation of 1-(2-bromophenyl)pyrrole with 2 equivalent of BuLi in ether at 0°. Some reactions of I were discussed. The benzenoid Li is more reactive towards electrophiles than the pyrrolic Li.

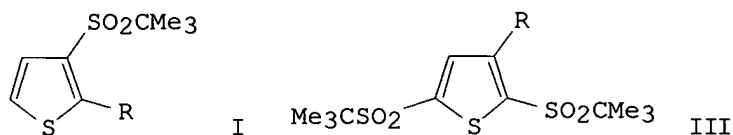
RX(1) OF 36



RX(2) OF 36

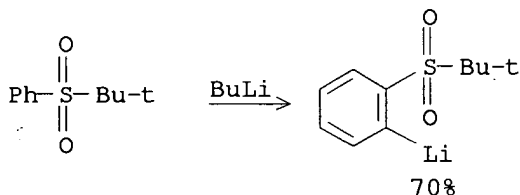


L6 ANSWER 51 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 90:151900 CASREACT  
 TITLE: Reactions of arylsulfonyl compounds with an excess of organolithium reagent. 13. Synthesis of o-mercaptosulfones and o-disulfones of benzene, naphthalene, and thiophene series based on o-lithiumsulfones  
 AUTHOR(S): Gol'dfarb, Ya. L.; Stoyanovich, F. M.; Chermanova, G. B.; Lubuzh, E. D.  
 CORPORATE SOURCE: Inst. Org. Khim. im. Zelinskogo, Moscow, USSR  
 SOURCE: Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1978), (12), 2760-7  
 CODEN: IASKA6; ISSN: 0002-3353  
 DOCUMENT TYPE: Journal  
 LANGUAGE: Russian  
 GI

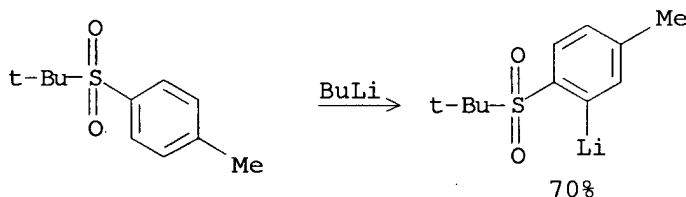


AB O-mercapto sulfones of the benzene, naphthalene and thiophenes and their transition metal salts were prepared. The IR showed the existence of the intramol. H bond in the mercaptosulfones; it also confirmed the participation of the sulfonyl groups in coordination with the metal in their metallic derivs. A series of o-bissulfones and trissulfones of the benzene and thiophene series were prepared; one of these sulfonyl groups was the principal possibility for nucleophilic substitution. Mercaptan I (R = SH) (II) was obtained in 79% yield by reaction of I (R = Li) with S. II was converted to 30-63% I (R = MeS, Me3CS) by reaction with the corresponding alkyl halides. The sulfides were oxidized to give 40.5-68% I (R = MeSO2, Me3CSO2). Treatment of thiophene III (R = H) with  $\text{LiN}(\text{CHMe}_2)_2$  at  $-40^\circ$  followed by S gave 79.5% III (R = SH). III (R = SO2CMe3) was obtained by successive treatment of 3-tert-butylthio-2,5-dilithiothiophene with S, MeS and  $\text{H}_2\text{O}_2$  in AcOH.

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RX(6) OF 49



L6 ANSWER 52 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 90:87536 CASREACT

TITLE: Metalation of aromatic tertiary diamines with n-butyllithium

AUTHOR(S): Friedmann, Gilbert; Linder, Pierre; Brini, Mathilde; Cheminat, Annie

CORPORATE SOURCE: Lab. Synth. Org., Inst. Chim., Strasbourg, Fr.

SOURCE: Journal of Organic Chemistry (1979), 44(2), 237-9

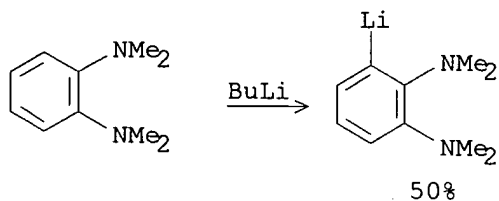
CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

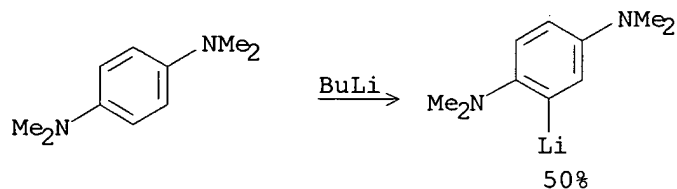
LANGUAGE: English

AB Lithiation of o- and p-(Me2N)2C6H4, and (p-Me2NC6H4)CH2 with BuLi in hexane at  $60^\circ$  gave 2,3- and 2,5-(Me2N)2C6H3Li and [3,4-Li(Me2N)C6H3]2CH2, resp.

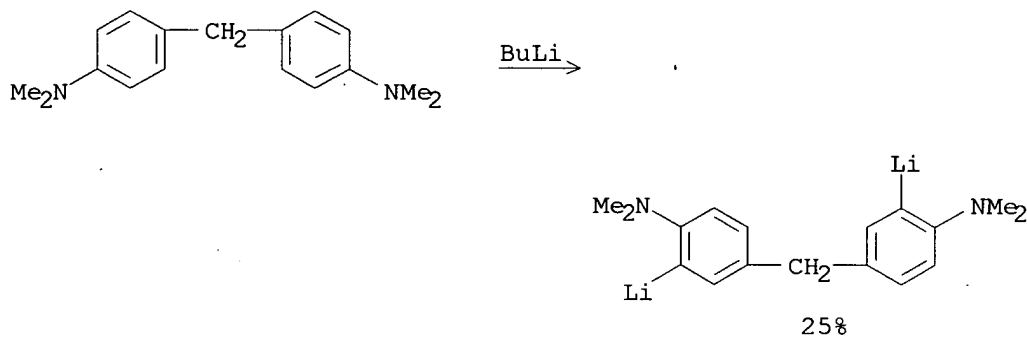
RX(1) OF 9



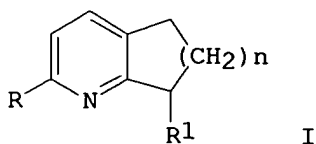
RX(3) OF 9



RX(5) OF 9



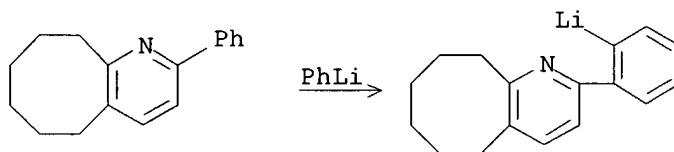
L6 ANSWER 53 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 85:46792 CASREACT  
TITLE: Lithiation of pyrido[b]cycloalkenes with phenyllithium  
AUTHOR(S): Epsztajn, J.; Bieniek, A.; Brzezinski, J. Z.  
CORPORATE SOURCE: Inst. Chem., Univ. Lodz, Lodz, Pol.  
SOURCE: Bulletin de l'Academie Polonaise des Sciences, Serie  
des Sciences Chimiques (1975), 23(11), 917-22  
CODEN: BAPCAQ; ISSN: 0001-4095  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
GI



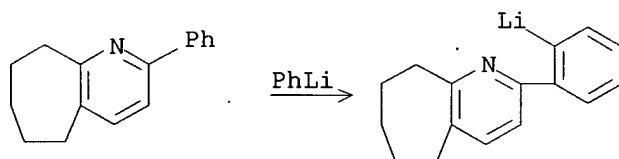
AB The direction of lithiation of pyrido[b]cycloalkenes I with PhLi in Et<sub>2</sub>O depended on the size of the cycloalkene ring. The relative reactivity of the C-H bond of the methylene group of the cycloalkene ring depends on the

ring size effect, i.e.  $n = 2 > n = 1$  and  $\text{Me} > \text{Ph} > n = 3 > n = 4$ . I (R = Ph, R1 = H, n = 1, 2) and 6-phenyl-2-picoline gave I (R = Ph, R1 = Li, n = 1, 2) and 2-lithiomethyl-6-phenylpyridine, resp., and I (R = Me, R1 = H, n = 2-4) gave I (R = Me, R1 = Li, n = 2) and I (R = LiCH<sub>2</sub>, R1 = H, n = 3, 4), resp. I (R = Me, R1 = H, n = 1) gave 1:1 I (R = Me, R1 = Li, n = 1) (II) and I (R = LiCH<sub>2</sub>, R1 = H, n = 1) instead of the expected II. Lithiation of I (R = Ph, R1 = H, n = 3, 4) initially gave I (R = o-LiC<sub>6</sub>H<sub>4</sub> R1 = H, n = 3, 4) which slowly rearranged to give I (R = Ph, R1 = Li, n = 3, 4).

RX(1) OF 4



RX(4) OF 4



L6 ANSWER 54 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 84:135202 CASREACT

TITLE: Selective halogen-lithium exchange in bromophenylalkyl halides

AUTHOR(S): Parham, William E.; Jones, Lawrence D.; Sayed, Yousry A.

CORPORATE SOURCE: Paul M. Gross Chem. Lab., Duke Univ., Durham, NC, USA

SOURCE: Journal of Organic Chemistry (1976), 41(7), 1184-6  
CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

LANGUAGE: English

GI For diagram(s), see printed CA Issue.

AB Exchange of the aryl halide atom in o-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl, o-BrC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>Br, and o-BrC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>Cl for Li was carried out with BuLi in THF-hexane at -100°. The stable lithio derivs. reacted with a variety of electrophiles; e.g., o-LiC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (I) with H<sub>2</sub>O, cyclohexanone, or PhNCO at low temperature gave, resp., PhCH<sub>2</sub>Cl, II, and III. I with H<sub>2</sub>O at room temperature

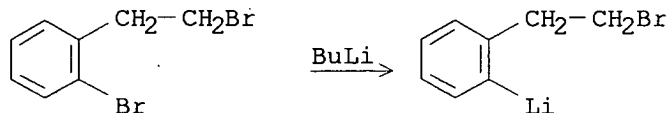
gave 9,10-dihydroanthracene (not benzocyclopropene). Benzocyclobutene was formed from o-LiC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>2</sub>Br under similar conditions. O-halobenzyl bromides were lithiated at the benzyl bromine atom and underwent subsequent coupling to bibenzyl. O-BrC<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>)<sub>3</sub>Br with BuLi underwent intramol. coupling to indan.



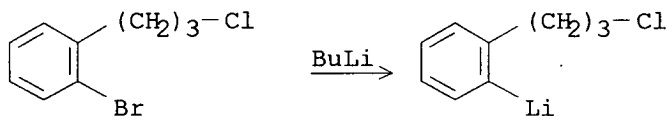
RX(4) OF 19



RX(6) OF 19

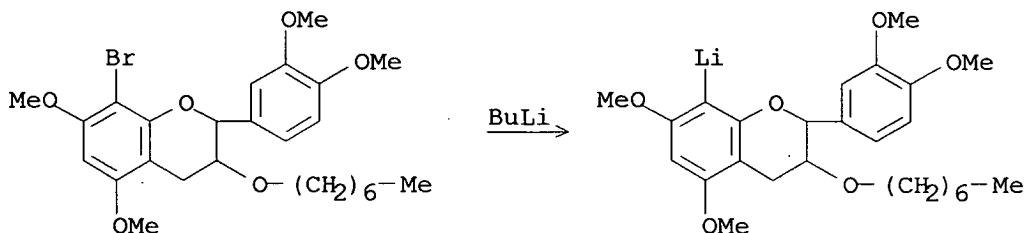


RX(8) OF 19



L6 ANSWER 55 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 67:11392 CASREACT  
TITLE: The structure of a C<sub>30</sub>H<sub>26</sub>O<sub>12</sub> procyanidin from cola nuts  
AUTHOR(S): Weinges, Klaus; Perner, Johannes  
CORPORATE SOURCE: Univ. Heidelberg, Heidelberg, Fed. Rep. Ger.  
SOURCE: Chemical Communications (London) (1967), (7), 351-2  
CODEN: CCOMA8; ISSN: 0009-241X  
DOCUMENT TYPE: Journal  
LANGUAGE: English  
GI For diagram(s), see printed CA Issue.  
AB cf. CA 63: 5588b. The structure of a procyanidin (I) isolated from cola nuts was confirmed by synthesis. Bromination of II (R = R' = H) gave II (R = Br, R' = H) which was benzylated to give II (R = Br, R' = PhCH<sub>2</sub>) (III). Treatment of III with BuLi gave II (R = Li, R' = PhCH<sub>2</sub>) which was condensed directly with IV followed by hydrogenolysis and acetylation to give I.

RX(1) OF 1

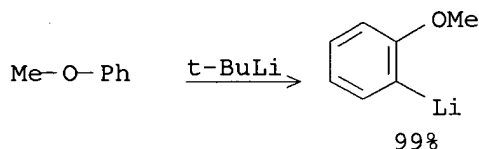


NOTE: Classification: Lithiation; Exchange; # Conditions: n-BuLi

L6 ANSWER 56 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
ACCESSION NUMBER: 65:65119 CASREACT  
TITLE: Steric effects in the metalation of some aromatic substrates with alkylolithium reagents  
AUTHOR(S): Hendrix, John Paul, Jr.

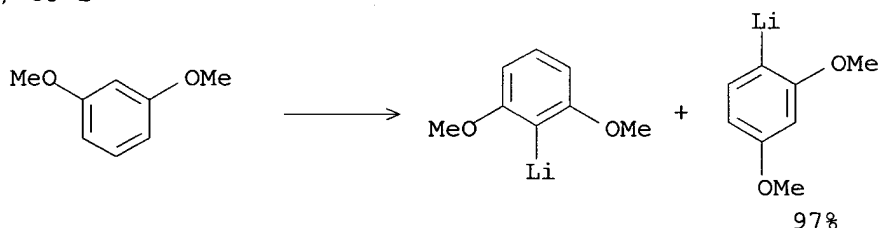
CORPORATE SOURCE: Univ. of Tennessee, Knoxville  
 SOURCE: (1966) 158 pp. Avail.: Univ. Microfilms (Ann Arbor, Mich.), Order No. 66-5346  
 From: Dissertation Abstr. 26(12), 7036  
 DOCUMENT TYPE: Dissertation  
 LANGUAGE: English  
 AB Unavailable

RX(1) OF 2



NOTE: Classification: Lithiation; Regioselective; # Conditions: t-BuLi

RX(2) OF 2



NOTE: Classification: Lithiation; Regioselective; # Conditions: n-BuLi;  
 # Comments: 97% of yield is 1,2,3-substituted product; 3% of yield is 1,4,3-substituted product

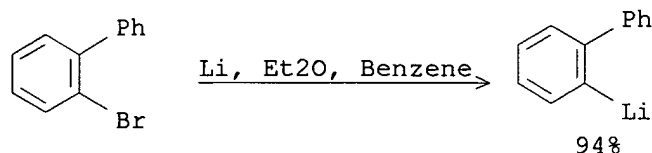
L6 ANSWER 57 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 52:113367 CASREACT  
 TITLE: Organotin compds. with bulky aryl groups. I. Tetra(2-biphenyl)tin, and the 3- and 4-isomers  
 AUTHOR(S): Bahr, Gerhard; Gelius, Rolf  
 CORPORATE SOURCE: Univ. Greifswald, Germany  
 SOURCE: Chemische Berichte (1958), 91, 812-18  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DOCUMENT TYPE: Journal  
 LANGUAGE: Unavailable

AB An Et<sub>2</sub>O-C<sub>6</sub>H<sub>6</sub> solution (175 ml.) containing 13.7 g. (2-biphenyl)lithium (cf. Bell, et al., C.A. 20, 2848; Campbell, C.A. 45, 6595b; Littlejohn and Smith, C.A. 48, 1749i; Zaheer and Faseeh, C.A. 39, 2913) is added in 0.5 hr., while stirring, to a solution of 4 g. SnCl<sub>4</sub> and 25 ml. dry C<sub>6</sub>H<sub>6</sub>. After evaporation of 75-100 ml. of the solvent, the solution is stirred, refluxed, and heated 2 hrs., hydrolyzed with Br water, separated, crystallized, dried, and recrystd. (boiling 1,2-Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) to produce a 71.2% yield of tetra(2-biphenyl)tin (I), m. 300-1°, insol. in Et<sub>2</sub>O and petr. ether, hard to dissolve in hot AcOEt, EtOH, or tetrahydrofuran. I is the most stable of the 3 isomers. Tetra(3-biphenyl)tin (II) made similarly, m. 145.5-5.8°, somewhat soluble in Et<sub>2</sub>O, soluble in C<sub>6</sub>H<sub>6</sub>, C<sub>5</sub>H<sub>6</sub>N, CHCl<sub>3</sub>, hot AcOEt, and hot ligroine. II is the least symmetrical and lowest melting of the 3. Tetra(4-biphenyl)tin (III), made in 77% yield, m. 268.5°, insol. in EtOH, difficultly soluble in Et<sub>2</sub>O, easily in hot ligroine, hot AcOR, hot CHCl<sub>3</sub> and hot C<sub>5</sub>H<sub>5</sub>N. I and HgCl<sub>2</sub> react to form (2-biphenyl)mercuric chloride, m. 166-7°. Di(2-biphenyl)tin chloride is produced by treating I with HCl. Tri(2-biphenyl)tin bromide, m. 107.5-8.0°, is made by treating (2-

biphenyl)magnesium bromide with SnBr<sub>4</sub> in a 4:1 molar ratio.

RX(1) OF 2



NOTE: Classification: Lithiation; Exchange; # Conditions: Li Et<sub>2</sub>O benzene; 1h; heat water bath; 1h-1h30mn

L6 ANSWER 58 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 52:104069 CASREACT

TITLE: Lithium sodium organic complexes. III. Anionization reactions with sodium diphenyllithium

AUTHOR(S): Wittig, Georg; Benz, Eberhard

CORPORATE SOURCE: Univ. Tübingen, Germany

SOURCE: Chemische Berichte (1958), 91, 873-82

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal

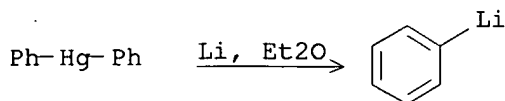
LANGUAGE: Unavailable

AB cf. C.A. 50, 1633d. Metalation reactions of CH<sub>2</sub>Ph<sub>2</sub> and phenolic ethers were described which showed the superiority of (Ph<sub>2</sub>Li)Na (I) over organic Li compds. and which confirmed the authors' conception that the mechanism was one of proton-metal exchange. Of particular interest was the conversion of Ph<sub>2</sub>S to dibenzothiophene (II) in improved yields. (% Metalation was determined by treatment with Ph<sub>2</sub>CO.) Ph<sub>2</sub>Hg (m. 124°) (12 g.) in 50 cc. absolute Et<sub>2</sub>O (all operations under N) and 1.8 g. Li clippings and some glass fragments shaken 20 hrs. gave a 1.3N Et<sub>2</sub>O solution of PhLi (salt-free) (solution III); 20 cc. N III 3.6 g. Ph<sub>2</sub>Hg in 110 cc. Et<sub>2</sub>O, 2 g. Na, and some broken glass shaken 2 hrs. gave a 0.15N solution of I (solution IV); 2 cc. N III, 3.6 g. Ph<sub>2</sub>Hg, and 4.5 g. Na wire in 50 cc. absolute Et<sub>2</sub>O shaken 2 hrs. with glass fragments gave a suspension of I (1:10 PhLi-PhNa) (the suspension was decanted from the amalgam for use) (solution V). To 20 millimoles CH<sub>2</sub>Ph<sub>2</sub> in 20 cc. absolute Et<sub>2</sub>O was added 66 cc 0.15N IV, the solution treated with Dry Ice after 90 min., and the product shaken with H<sub>2</sub>O to give 7% CHPh<sub>2</sub>CPh<sub>2</sub>OH (VI), m. 229-30° (EtOH) (as a precipitate), 61% CH<sub>2</sub>Ph<sub>2</sub>, b<sub>12</sub> 128-30° (from the Et<sub>2</sub>O phase), 0.3 g. BzOH, and Ph<sub>2</sub>C(CO<sub>2</sub>H)<sub>2</sub> (VII), m. 143-4° (decomposition) (di-Me ester, m. 93°), converted by heating to CHPh<sub>2</sub>CO<sub>2</sub>H (VIII), m. 146°. In a 2nd experiment, 10 millimoles CH<sub>2</sub>Ph<sub>2</sub> in 10 cc. absolute Et<sub>2</sub>O and 33 cc.

0.15N IV

kept 16 hrs. under N, poured on Dry Ice, and worked up as above gave 26% VII and 23% VIII. In a 3rd experiment Ph<sub>2</sub>CO added to the mixture after 16 hrs. gave 53% VI, 40% CH<sub>2</sub>Ph<sub>2</sub>, Ph<sub>2</sub>CO, and 25% Ph<sub>3</sub>COH (IX). PhOMe (16 millimoles) and 8 millimoles IV in 63 cc. Et<sub>2</sub>O treated with 16 millimoles Ph<sub>2</sub>CO after 3 hrs. (the Et<sub>2</sub>O boiled up), the mixture hydrolyzed, the Et<sub>2</sub>O removed, the residue extracted with petr. ether to remove Ph<sub>2</sub>CO, and the remaining mixture (3.1 g.) chromatographed on Al<sub>2</sub>O<sub>3</sub> gave, on elution with C<sub>6</sub>H<sub>6</sub>, 23% o-MeOC<sub>6</sub>H<sub>4</sub>CPh<sub>2</sub>OH (X), m. 127-9°, and on further elution with CHCl<sub>3</sub> 49% IX, m. 159-60°. A similar experiment in which Ph<sub>2</sub>O was added after 48 hrs. gave 71% X. In a further experiment V (2 millimoles PhLi-20 millimoles PhNa) and 22 millimoles PhOMe in 50 cc. Et<sub>2</sub>O shaken 3 hrs. and treated with 20 millimoles Ph<sub>2</sub>CO gave 40% X, m. 126-7°, and 46% IX, m. 158-9°. p-BrC<sub>6</sub>H<sub>4</sub>OMe (16 millimoles) and 8 millimoles IV in 63 cc. Et<sub>2</sub>O treated with 16 millimoles Ph<sub>2</sub>CO after 10 min., the mixture hydrolyzed, the Et<sub>2</sub>O phase worked up, and the residue

recrystd. from MeOH gave 1.1 g. [5,2-Br(MeO)C<sub>6</sub>H<sub>3</sub>]CPh<sub>2</sub>OH (XI), m. 125-6°; the MeOH-soluble fraction chromatographed on Al<sub>2</sub>O<sub>3</sub> in 1:10 C<sub>6</sub>H<sub>6</sub>-cyclohexane (XII) and eluted with the same solvent mixture gave 3% Ph<sub>2</sub>, m. 68-9° (EtOH), and 5% 4-MeOC<sub>6</sub>H<sub>4</sub>Bz, m. 86-7° (petr. ether); continued elution with C<sub>6</sub>H<sub>6</sub> gave 4% 4-MeOC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>OMe-4, m. 170-2°, and 1.2 g. XI, m. 126-7°; further elution with CHCl<sub>3</sub> gave 11% IX and then 8% 4-MeOC<sub>6</sub>H<sub>4</sub>CPh<sub>2</sub>OH, m. 78-9° (petr. ether-Et<sub>2</sub>O). Ph<sub>2</sub>S (20 millimoles) and 10 millimoles IV in 86 cc. Et<sub>2</sub>O kept 20 hrs. at room temperature, treated with 20 millimoles Ph<sub>2</sub>CO, hydrolyzed, the Et<sub>2</sub>O phase distilled, unreacted Ph<sub>2</sub>S (55%) distilled, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 33% IX, m. 156-8°, 26% 2-[Ph<sub>2</sub>C(OH)]C<sub>6</sub>H<sub>4</sub>SPh (XIII), m. 142-3°, and 4.5% {2-[Ph<sub>2</sub>C(OH)]C<sub>6</sub>H<sub>4</sub>S}<sub>2</sub> (XIV), m. 204.5-5.5°. XIII in boiling AcOH treated with a few drops of concentrated HCl cyclized and gave 10,10-diphenylthiaxanthine, m. 210-11° (EtOH). XIV treated similarly gave 4-(diphenylacetoxymethyl)-10,10-diphenylthiaxanthine, m. 306-8° (EtOAc). In a further experiment, 18 millimoles Ph<sub>2</sub>S and 9 millimoles IV in 80 cc. Et<sub>2</sub>O kept 4 days at room temperature and then heated at 60° for 4 days, the mixture decanted from precipitated NaH into H<sub>2</sub>O, the Et<sub>2</sub>O layer extracted with 20% aqueous NaOH (from the alkaline extract was isolated 90 mg. PhSH), the Et<sub>2</sub>O distilled, and the residue pressed and recrystd. from EtOH gave 3.2 g. II, m. 97-8°. Ph<sub>3</sub>N (18 millimoles) and 9 millimoles IV in 60 cc. Et<sub>2</sub>O kept 2 weeks at room temperature (no separation of NaH observed), poured on Dry Ice, the reaction product extracted with Et<sub>2</sub>O, and the extract distilled gave 82% recovered Ph<sub>3</sub>N; the aqueous phase acidified gave 1 g. mixture which, after extraction of BzOH with XII, left 11% crude (2-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>NPh (XV), m. 223-4° (decomposition) (dilute EtOH). 2-PhNHC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H (XVI) (1.5 g.), 2.6 g. 2-IC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me, 2 g. K<sub>2</sub>CO<sub>3</sub>, and 0.5 g. Cu (Naturkupper C) in 1 cc. xylene heated 11 hrs. at 190°, the mixture extracted with dry Et<sub>2</sub>O, boiled 30 min. with 10% aqueous KOH, the solution filtered, the filtrate acidified, and the precipitate recrystd. from HCO<sub>2</sub>H gave 0.82 g. XV, m.p. and mixed m.p. 224-5° (decomposition). Similarly XVI and 3-IC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>Me gave (2-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)(3-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>)NPh, m. 224.5-5.5°, mixed m.p. with XVI depressed. Ph<sub>3</sub>As (18 millimoles) and 9 millimoles IV in 60 cc. Et<sub>2</sub>O kept 2 weeks at room temperature (NaH separated), hydrolyzed, filtered, the Et<sub>2</sub>O layer distilled, the residue taken up in XII, chromatographed on Al<sub>2</sub>O<sub>3</sub>, eluted with XII (30% Ph<sub>3</sub>As recovered), and then eluted with C<sub>6</sub>H<sub>6</sub> gave 4% phenylbiphenylenearsine, m. 84-5° (EtOH). Anthracene (XVII) (7.4 g.) and 0.8 g. Mg turnings in 35 cc. tetrahydrofuran (XVIII) [dried over Ph<sub>2</sub>CONa] treated after gentle warming with 1/4 of 5.3 g. o-FC<sub>6</sub>H<sub>4</sub>Br (m. -35°) in 15 cc. absolute XVIII under N, the remaining solution added dropwise with stirring after the initiation of the reaction while maintaining the temperature at 60°, boiled 90 min., the warm solution poured into MeOH (XVII precipitated), the solution evaporated (lastly in vacuo), the residue extracted twice with 50 cc. hot H<sub>2</sub>O containing some HCl, filtered off and dried in vacuo, the solid in 45 cc. hot xylene boiled 20 min. with 5 g. maleic anhydride, and the product filtered off gave 7.8 g. adduct, m. 256-8°; the filtrate boiled 2 hrs. in 80 cc. 2N NaOH, washed, dried, and xylene removed gave 4.1 g. oily crystals (XIX); XIX digested with petr. ether (b. 50-70°), the residue (2.8 g.) dissolved in 70 cc. CCl<sub>4</sub>, chromatographed on 280 g. acid Al<sub>2</sub>O<sub>3</sub>, and the CCl<sub>4</sub> removed gave 2.14 g. triptycene, m. 255.0-6.5° (from XII). The column then eluted with C<sub>6</sub>H<sub>6</sub> gave 11% triphenylene, m. 194-5° (CCl<sub>4</sub>). The mechanisms of these reactions are discussed.



NOTE: Classification: Lithiation; Transmetalation; # Conditions: Li Et<sub>2</sub>O /N2 20h; # Comments: product in 1.3N Et<sub>2</sub>O solution

L6 ANSWER 59 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 52:1753 CASREACT

TITLE: Dimerization of 4-isopropenylphenyl methyl sulfide with 43% sulfuric acid

AUTHOR(S): van der Zanden, J. M.; Nieuwenhuis, J.; Bos, H. J. T.

CORPORATE SOURCE: State Univ., Groningen, Neth.

SOURCE: Recueil des Travaux Chimiques des Pays-Bas et de la Belgique (1957), 76, 669-73

CODEN: RTCPB4; ISSN: 0370-7539

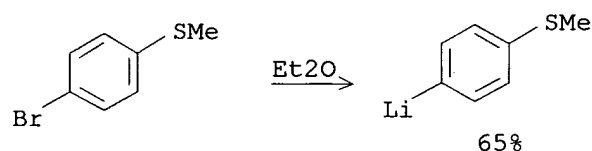
DOCUMENT TYPE: Journal

LANGUAGE: Unavailable

AB C.A. 51, 11301c. On boiling with 43% H<sub>2</sub>SO<sub>4</sub>, 4-(CH<sub>2</sub>:CMe)C<sub>6</sub>H<sub>4</sub>SMe (I) dimerized more slowly than 4-(CH<sub>2</sub>:CMe)C<sub>6</sub>H<sub>4</sub>OMe (II) and about as rapidly as CH<sub>2</sub>:CMePh under the same conditions. Filtered BuLi in Et<sub>2</sub>O (from 137 g. BuBr and 18 g. Li in 2 l. absolute Et<sub>2</sub>O) treated quickly with stirring with 89 g. p-BrC<sub>6</sub>H<sub>4</sub>SMe in 800 ml. Et<sub>2</sub>O, the mixture kept 15 min. at room temperature and cooled to 0°, treated dropwise in 25 min. with 60 g. Me<sub>2</sub>CO in 100 cc. absolute Et<sub>2</sub>O and the mixture kept 2 hrs., the suspension neutralized with 2N HCl and the Et<sub>2</sub>O layer washed with aqueous NaHCO<sub>3</sub> and H<sub>2</sub>O, the dried extract evaporated, distilled to remove 40 g. BuMe<sub>2</sub>COH, b<sub>15</sub> 50-1°, and the residual crystalline mass recrystd. from MeOH gave 47 g. I, m. 49-50°. I (15 g.) boiled 7 hrs. with stirring with 130 ml. 43% H<sub>2</sub>SO<sub>4</sub>, the cooled mixture poured onto ice and extracted with Et<sub>2</sub>O, the washed and dried extract evaporated, and the residue fractionated (N atmospheric) yielded 67% dimer (III), b<sub>4</sub> 256-8°, n<sub>20D</sub> 1.6307. III (6 g.) in 600 ml. Me<sub>2</sub>CO treated 1 week with 20 g. KMnO<sub>4</sub> with occasional shaking, the brown suspension filtered off, the filtrate evaporated, and the residual oil (3 g.) treated with 2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NHNH<sub>2</sub> in alc. H<sub>2</sub>SO<sub>4</sub> to give authentic p-methylthioacetophenone 2,4-dinitrophenylhydrazone, m. 231.0-1.5°; the precipitate suspended in 50 ml. H<sub>2</sub>O and clarified with SO<sub>2</sub>, the warm solution filtered and cooled, filtered, and the crystalline precipitate (1.5 g.) crystallized from 50% alc. and twice from H<sub>2</sub>O gave α-(p-methylsulfonylphenyl)isobutyric acid (IV), m. 182.3°. Condensation of MeSPh and ClCH<sub>2</sub>OMe according to Buu-Hoi and Ho. act. an (C.A. 47, 1634d) yielded 10.5% p-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Cl (V), b<sub>12</sub> 136-8°, n<sub>20D</sub> 1.6051. V (10 g.) in 225 ml. 96% alc. refluxed 4.5 hrs. with 21.2 g. NaCN in 55 ml. H<sub>2</sub>O and evaporated in vacuo, the residue diluted with 300 ml. H<sub>2</sub>O and extracted with Et<sub>2</sub>O, the dried extract evaporated, and the residue distilled gave 4.8 g. colorless liquid, b<sub>1.0</sub> 118-31°, and material, b<sub>1.0</sub> 131-54°. Redistn. of the colorless liquid yielded 3.1 g. p-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CN (VI), b<sub>1.0</sub> 120.5-7.5°, n<sub>20D</sub> 1.5827,  $\nu$  2240, 3450 cm.<sup>-1</sup> The latter band showed contamination of VI with p-MeSC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>OH. Recrystn. of the semisolid material from petr. ether yielded 100 mg. pure VI, m. 40.5-1.5°,  $\nu$  2240 cm.<sup>-1</sup>. VI (2.8 g.) in 10 ml. Et<sub>2</sub>O added slowly with stirring to NaNH<sub>2</sub> (from 0.99 g. Na in 30 ml. Et<sub>2</sub>O) and the mixture kept 2 hrs. at room temperature, the mixture refluxed 1.5 hrs. and cooled to

0°, 3.35 g. MeI in 5 cc. Et2O added and the mixture boiled 10 min., the cooled mixture treated with 3.35 g. MeI in 5 cc. Et2O and refluxed 10 hrs., the mixture diluted with H2O and extracted with Et2O, the oily prod boiled 6 hrs. with 50 ml. HO(CH2)2OH, 2 ml. H2O, and 2 g. KOH and the mixture poured into H2O, the solution extracted with Et2O and the extract treated with NaNO2 and HCl, the extract washed with 2N NaOH and the alkaline washings added to the original KOH solution, the alkaline solution acidified and extracted with Et2O, the pale brown oily product purified with 30% H2O2 in AcOH, and the colorless product recrystd. from H2O gave 0.22 g. IV. A mechanism was proposed for the dimerization. I dimerized more slowly than II as a consequence of the pos. electromeric effect (+E), which is smaller with the MeS than with the MeO group. Since the +E effect of the MeSC6H4 group differs only slightly from that of the Ph group the rates of dimerization of I and CH2:CMcPh are almost identical.

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NOTE: Classification: Lithiation; Exchange; # Conditions: n-BuLi Et2O; 20 deg 15mn; # Comments: yield >65%

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---Logging off of STN---

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Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	493.96	494.17
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	-45.00	-45.00

STN INTERNATIONAL LOGOFF AT 11:19:48 ON 13 MAY 2008

L6 ANSWER 8 OF 59 CASREACT COPYRIGHT 2008 ACS on STN  
 ACCESSION NUMBER: 127:5187 CASREACT <<LOGINID::20080513>>  
 TITLE: Preparation of aryllithium in ether solutions using  
 Lewis bases  
 INVENTOR(S): Schwindeman, James A.; Sutton, Douglas E.; Morrison,  
 Robert C.; Stryker, Sonia S.  
 PATENT ASSIGNEE(S): FMC Corp., USA  
 SOURCE: U.S., 4 pp.  
 CODEN: USXXAM  
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 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5626798	A	19970506	US 1996-587813	19960105
WO 9725334	A1	19970717	WO 1996-US7624	19960524
W: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN				
RW: KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9658036	A	19970801	AU 1996-58036	19960524
DE 19681729	T0	19981217	DE 1996-19681729	19960524
DE 19681729	C2	20001116		
PRIORITY APPLN. INFO.:			US 1996-587813	19960105
			WO 1996-US7624	19960524

OTHER SOURCE(S): MARPAT 127:5187

AB An improved process for producing high purity solns. of aryllithium compds. and the product solns. are claimed. The process comprises reacting a particulate alkali metal having a particle size of 10-300  $\mu$ m, with an aryl halide in a normally liquid ethereal solvent ROR1, wherein R and R1 are selected from the group of alkyl radicals containing from 3 to 6 C atoms, in the presence of a Lewis base selected from compds. of the formula: R2AR3(R4)z and cyclic -(CR5R6)y-(A(R4)z)- wherein A is selected from O, N, P or S; R2, R3, and R4 are selected from alkyl radicals containing from 1 to 6 C atoms; R5 and R6 are independently selected from H or alkyl radicals containing one to six C atoms; y = 4 to 6; but when A is O or S, z = 0; and when A is N or P, z = 1, and provided there is a mole ratio of ether to aryl halide of at least 1.3 to 1 and a mole ratio of Lewis base to aryl halide of from 0.01 to 0.5. For example, to a reaction flask containing 1.25 mol Li powder and 0.94 mol Bu2O was added, dropwise, over a period of 60 min, a solution of 0.52 mol PhCl and 0.052 mol MeOtBu, while maintaining the reaction temperature at 30-35°; the yield of PhLi was 87.4%. If no MeOtBu was present, the yield was 80.8% and the reaction was slower (16% PhCl remaining after 120 min vs. 6%).

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